Advances
in the utilization of
waste materials
and
alternative sources of energy
in clay brick making
-
A South Tyrolean case study investigating environmental and financial impacts

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A thesis submitted in partial fulfillment of the requirements of
Staffordshire University for the degree of Doctor of Philosophy

December 2010

DECLARATION

I hereby declare that this thesis is my own work and that I have not submitted it for any other degree to any other university.

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Acknowledgements

My special thanks go to Prof. Dr. Michael Anderson and Prof. Dr. Glynn Skeratt of Staffordshire University. Special thanks are also due to Dr. Paul Gasser of Ziegel Gasser Mattoni.

Important roles in this work have played my friends and colleagues at the Vela Borgonato and the Vela San Giovanni del Dosso brick plants, at the SBBC brick plant in Morocco and my former colleagues at the Gasser brick plant in Sciaves. I am grateful to all of them for the many hours of fruitful and pleasant researching, experimenting and working together and for sharing their immense and invaluable practical knowledge and skills with me.

I would like to extend thanks to Mrs. Zineb Addioui of SBBC Societè Briqueterie Bati Chouia and Mr. N. Criscuolo and Dr. P. Morelli of Recuperi Industriali S.r.l.. Not forgotten shall be Mr. Felix Ast, who assisted me in some of the research and development work in continuation of the original work at Gasser, and Mr. M. El Eulj of SBBC Societè Briqueterie Bati Chouia.

This thesis is dedicated to my mother Hildegard and to the memory of my late father Walter.

Abstract

The background to this research program was the need to investigate novel technologies and their application to fired ceramic processes that would facilitate the return to profitability for a small size brick maker. The company, Gasser Brick Company. Ziegel Gasser Mattoni GmbH S.r.l., in Natz-Schabs (Naz-Sciaves) in the north of Italy, is a relatively small manufacturer producing < 20,000 metric tons of brick per year. In this thesis the economic, environmental and social advantages consequent to a complete review of the approach to the company's manufacture of cored clay bricks are discussed, including energy saving measures and the use of novel fuel and clay body supplements. A number of wide ranging novel technical modifications to the production processes of the Gasser Brick company have been tested, evaluated, reviewed, compared, and critically evaluated. The approach includes the utilization of a substantial percentage of various wastes as part-substitution of, or as an addition to, quarried raw materials and also the use of renewable and alternative fuels as a substitute for fossil fuels.

A number of these modifications have resulted in beneficial changes to the product and the efficiency of the production process and considerably reduced the environmental footprint of the operation. Process modifications and the technological improvements to production equipment are explained and discussed along with detailed information about the measures that enabled the Gasser Brick company to return the profitability.

The modifications resulted in a substantial increase of income. Revenues from waste gate fees are about 30% of the total turnover of the company. Costs for thermal energy dropped by 2/3: A ton of boiler oil commanded a price of 220 - 245 €/ton versus the around 80 €/ton of rendering fat.

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Abbreviations and Acronyms

AFNOR	Association française de Normalisation (http://www.afnor.org/)
AIMCC	Association des Industries de Produits de Construction.(http://www.aimcc.org)
Anaerobically digested sewage sludge	Raw sewage sludge that has been subjected to an anaerobica digestion process breaking down the organic content of the sludge.
ANDIL ASSOLATERIZI	Associazione nazionale degli industriali dei laterizi (http://www.laterizio.it/)
ANPA	Agenzia Nazionale per la Protezione Ambientale – Italian National Environment Agency (later ISPRA)
AP	Acidification potential
APAT	Agenzia per la Protezione dell'Ambiente ed i servizi Tecnici alian National Environment Agency (formerly ANPA, later ISPRA)
ASTM	American Society for Testing and Materials (http://www.astm.org/)
AUB	Arbeitsgemeinschaft umweltverträgliches Bauprodukt e.V. (now: Institut Bauen und Umwelt e. V. (IBU))
BEA	British Electricity Authority (dissolved in 1955)
BIOTON	Registered trademark of Ziegel Gasser Mattoni GmbH S.r.l.
Body fuel (brick making jargon)	Fuel or energy rich combustible material contained in a ceramic body
Body fuel (brick making jargon)	Combustible matter added to the feed used in making brick.
Boustead	Boustead Consulting Ltd. - company offering database and software for LCA calculation
BRE	Building Research Establishment – manages the “Green Book Live” EPD scheme (http://www.bre.co.uk/)
Brick/Air value (brick making jargon)	The quantitative relationship between weight of brick in a kiln and weight of air expelled from the kiln per unit of time, generally per hour, from the stack.
CAS	Chemical Abstract Service (http://www.cas.org/)
CEGB	Central Electricity Generating Board (privatized in 1990)
Cell (brick making jargon)	Large core or area of void.
CEN	Comité Européen de Normalisation – European Committee for Standardization (http://www.cen.eu/cenorm/homepage.htm)
CEN BT/WG	Working group which's role has been specified by the CEN Technical Board (BT)
CEN EN 832	Thermal performance of buildings. Calculation of energy use for heating. Residential buildings (withdrawn and substituted with ISO 13790:2008)
CEN/TC	European Committee for Standardization/ Technical Committee
CEN/TC 350	Technical Committee in charge of drafting a standardised voluntary approach for the delivery of environmental information on construction products, and to assess the environmental performance of buildings, and more generally the integrated performance of buildings.
CERAM	BRITISH CERAMIC RESEARCH LTD. Founded in 1920, provides materials analysis, research and quality testing to industry (http://www.ceram.com/)
Cerame-Unie	Association of the European Ceramics Industry (http://www.cerameunie.eu/)
Chamotte	Sometimes also named firesand is a generally porous, low density ceramic raw material obtained by firing clays, mostly fire clays, to high temperatures. The product is then ground to a desired particle size. Chamotte is sometimes found as product of the spontaneous combustion of, for example, oil shale mining waste tips (Grube Messel in Germany).
Clamp kiln (Scove kiln)	Field kiln usually built on a leveled refractory surface in varying shapes and sizes. The brick to be fired are stacked usually in a tapered fashion with a certain horizontal distance to each other to allow for air flow around the bricks. In the lower levels firing tunnels are provided. Clamp kilns can be fired with any solid fuel.
Cloud point	Temperature at which in a fuel wax begins to form.
C/N ratio	Carbon to nitrogen ratio - used in biogas technology to determine the suitability of a given substrate
Core (brick making jargon)	In brick making a core is defined as a single area of void of a brick induced by mainly extrusion through a die. Usually a core is, by dimension, a relatively limited cavity.
Cored brick (brick making jargon)	A clay building block with a number of cavities in it in direction of extrusion of the brick itself.

CORISO	Trademark UNIPOR for thermal insulation brick (http://www.unipor.com/index.php?id=17)
CRT	Cathode ray tube
CSTB	Centre Technique et Scientifique du Batimen (http://international.cstb.fr/)
D.A.CH (DACH) (brick making jargon)	Acronym – common designator for joint ventures between the German – Austrian and Swiss brick making associations.
De-inking	A process used in the recycling of waste paper where most of the printing ink and other impurities are removed to allow it to be re-used in the production of new paper. A chemical process using alkali and detergents is used. The recovered paper is first dissolved in water and separated from the non-fibre impurities. The fibres are then progressively cleaned in order to obtain the pulp and during this stage the ink is removed in a flotation process where air is blown into the solution. The ink adheres to bubbles of air and rises to the surface from where it is separated. After the ink is removed, the fibre may be bleached, usually with hydrogen peroxide
Dioxin	In the context of emissions into air it is more appropriate to define this class of polyhalogenated compounds as polychlorinated dibenzodioxins or PCDDs. They are toxic environment pollutants.
DTA	Differential thermal analysis.
Efflorescence (brick making jargon)	Visible effect of migration of salts, sulfates or sulphites to the surface of the brick
EN	Euronorm – European Standard
EN 771.1	European Standard for Clay Masonry Units
End shell (brick making jargon)	The side connecting one brick to the other
ENEL	Ente Nazionale per l'Energia Elettrica – an Italian energy provider
EP	Eutrophication potential
EPA	European Patent Agency
EPD	Environmental Product Declaration
Eutectic	A mixture at such proportions whose melting point is lower than that of any other mixture composed of the same constituents in different proportions.
Face (brick making jargon)	The side of the brick exposed to the view or to the rendering
FBA	Furnace bottom ash
Flux	A substance that lowers the melting or softening temperature of the mix or compound in which it is present. The degree of melting that occurs depends on the particle size of the powders present and the melting temperature of the individual particles. It also depends on whether material particles present are premelted and whether they soften or melt suddenly. Fluxing oxides are those of the RO group and include ones like K_2O, Na_2O, CaO, Li_2O, MgO. B_2O_3 is actually considered a glass former but it is also regarded as a flux by virtue of its low melting temperature.
Frit	In general a ceramic glass that has been premixed from raw powdered minerals and then melted, cooled by quenching in water, and ground into a fine powder. There are many advantages to using frits in glazes, enamels, ceramic bodies etc.-They are used to render soluble materials insoluble , to improve process safety of toxic metals, to reduce melting temperature and improve melt predictability, to avoid volatilization of unstable substances and to achieve oxide blends that are difficult or impossible with raw materials.
Fuller’s Earth	A clay material usually used to filter oils
Furan	A group of halogenated organic compounds more properly defined as chlorinated dibenzofuranes or PCDFs, in this context, are toxic environmental pollutants generally found in association with polychlorinated dibenzodioxins and are formed generally at temperatures below 1,200°C.
GaBi	Database and software for LCA calculation (http://www.gabi-software.com/)
Gasser.	Italian brick manufacturer. (http://www.ziegelgassermattoni.com/) Ziegel Gasser Mattoni GmbH S.r.l.
GBC	Green Building Challenge Handbook - report commissioned by the clay brick associations of Germany, Austria and Switzerland. Available online at (http://www.ziegel.at/gbc-ziegelhandbuch/default-eng.htm
Giavarini	Italian brick manufacturer. (http://www.giavarini.it/sites/0/IT/default.tpl) Laterizi Giavarini S.p.A.
Grog	A previously fired ceramic material that is finely ground and might be used to reduce shrinkage and improve drying.
GWP	Global warming potential
Hollow brick (brick making jargon)	In brick making a hollow brick is defined as a brick with a percentage of voids, depending on local custom, < 25% but < 35 to 47%.
Human toxicity	Characterization of toxic chemicals with relevance to human exposure based on the potential human toxicological effects expressed as critical volume i.e. the volume of a certain media required to absorb a specific emission without resulting in adverse effects.

Hüning	German brick manufacturer. (http://huening.mediatecs.de/start.php). Baustoffwerke Hüning GmbH
Hydrolization	Splitting of water molecule into hydrogen and hydroxide ions that might participate in further reactions.
IBU	Institut Bauen und Umwelt e. V. ((http://bau-umwelt.de/hp1/Startseite.htm)
INIES	Base de données française de référence sur les caractéristiques environnementales et sanitaires des produits de construction – French EPD declarations database. A joint venture between AFNOR, CSTB and other industrial associations (http://www.inies.fr/)
Iprona	Producer of fruit concentrates and puree /pulp concentrates of berries and tropical fruits and natural colorings (especially from elderberries) (http://www.iprona.com/) Iprona AG S.p.A.
ISO	International Standards Organization. Descriptions of ISO standards are, if available, the original ISO descriptions of content and applicability.
ISO 13790	ISO 13790 gives calculation methods for assessment of the annual energy use for space heating and cooling of a residential or a non-residential building, or a part of it, referred to as “the building”.
ISO 14000	A standard for environmental management
ISO 14020	Environmental labels and declarations -- General principles
ISO 14021	Type II environmental label.
ISO 14024	Type I environmental label.
ISO 14025	Type III environmental declaration.
ISO 14040	LCA principles and framework
ISO 14041	LCA Goal and scope definition and life-cycle inventory analysis (obsolete)
ISO 14042	LCA Life-cycle impact assessment (obsolete).
ISO 14043	LCA Life-cycle interpretation (obsolete).
ISO 14044	LCA Requirements and guidelines.
ISO 9000	A family of standards for management systems
ISPRA	Istituto Superiore per la Protezione e la Ricerca Ambientale ((http://www.isprambiente.it/site/it-IT/)
IZF e.V.	Institut für Ziegelforschung Essen e.V. Founded in 1952, provides materials analysis, research and quality testing to the brick industry.
JUWÖ Jungk	German brick manufacturer. (http://www.juwoe.de/). JUWÖ Poroton Werke Ernst Jungk und Sohn GmbH
Kieselguhr	Diatomaceous earth, a naturally occurring, soft, sedimentary rock with high porosity
LCA	Life Cycle Assessment, in general, if not differently specified, a cradle to grave analysis of the overall environmental impacts of a product or service.
LNG	Liquified natural gas
MRPI	Stichting Milieurelevante productinformatie – manages an EPD scheme in The Netherlands (http://www.mrpi.nl/)
MSWI	Municipal solid waste incineration
NG	Natural gas
ODP	Ozone depletion potential
OHSAS 18000	OHSAS 18000 is an international occupational health and safety management system specification. It comprises two sections, 18001 and 18002
ÖQS	Quality Austria GmbH – certification body
PAH	Polycyclic aromatic hydrocarbon
PAN	Pan Surgelati Srl – producer of deep frozen strudel (http://www.pan.it/)

PCB	Polychlorinated biphenyl – organic compounds with 1 to 10 chlorine atoms attached to byphenyl with the general chemical formula $C_{12}H_{10-x}CL_x$ where x is a value between 1 and 10.
PCR	Product Category Rule A set of rules, requirements and guide lines for developing Type III ISO 14025:2006 compliant environmental declarations for one or more product categories
Percentage of void (brick making jargon)	The total area of the cores and cells is defined as percentage of voids and classed as full brick, percentage of voids inferior to 20% of the total surface of the brick, perforated brick with less than 45% of voids area, and low density brick with up to 65%, or even more, of area of voids.
Perlite	An usually used in its expanded form, typical bulk density 30–150 kg/m^3, an amorphous volcanic glass that prior to its expansion by a thermal process in a purpose built kiln at temperature sof 850°C to 950°C, has a high water content
PFA	Pulverised fuel ash
Phenol	A toxic and antiseptic, white solid aromatic compound with a limited solubility in water and known also as carbolic acid
PM_{10}	Airborne particulate matter of 10 micrometers or less. Sources of particulate matter can be anthropogenic or natural.
$PM_{2.5}$	Airborne particulate matter of 2.5 micrometers or less. Sources of particulate matter can be anthropogenic or natural.
POCP	Photochemical ozone creation potential.
Polymeric organic compounds	E.g.: Carbonaceous substances of extremely high compound polarity and/or high molecular weight (Polymeric organic compounds have been added to soils for many years in attempts to control erosion and to adsorb organic contaminants)
Polysaccharide	Polymeric, linear or sometimes branched, carbohydrate structures formed of repeating units joined together by glycosidic bonds.
POP	Persistent Organic Compounds -chemical substances that persist in the environment, bio-accumulate through the food web, and pose a risk of causing adverse effects to human health and the environment
Pore-forming agent (brick making jargon)	Usually an organic substance that on firing of the clay body is combusted leaving voids within the clay body itself.
Porodur	Thermal sewage sludge recycling process.
PrEN	Preliminary Euronorm – preliminary European Standard
PSR	Product Specific Rule
R – Value	thermal resistance of a partition or wall system expressed in K * m^2/W. The R-value is the reciprocal of the U value .The higher the R-Value, the less heat is transmitted throughout the material.
Raw sewage sludge	Sludge from the treatment of waste waters.
Recuperi Industriali S.r.l.	Italian waste into brick raw material recycler. www.recuperindustriali.it
Rendering fat	Fat or tallow of animal origin.
Rimmele	German brick manufacturer. (http://rimmele.de)
RINA	The operational company of Registro Italiano Navale which was founded in Genova in 1861. The date of its establishment makes it one of the oldest classification societies in the world. RINA S.p.A. and its subsidiary companies mainly operate in the fields of ship classification, certification and advanced services to industry. (http://www.rina.org/)
RTS	Rakennustietot - Building Information Foundation (Finland). Manages an ISO compliant EPD scheme
SA 8000	The Social Accountability SA 8000 system is intended to promote human rights for workers and a complimentary instrument to fill current voids in the protection of workers
SAI	Social Accountability International - a non-governmental, international, multi-stakeholder organization dedicated to improvingworkplaces and communities by developing and implementing socially responsible standards.
SBBC	Societè Briqueterie Bati Chouia, Berechid, Marocco.
SBI	Statens Byggeforskningsinstitut (Danish Building Research Institute) (http://www.sbi.dk/)
Seger cone	A pyramid shaped cone of a definite admixture of lay and refractory materials that collapses at at a pre-defined temperature. Seger cones are available in definite temperature intervals and hence can be used to control absolute temperatures in a firing process. Named after Hermann Seger, 1839 - 1893, a German ceramist

Setting density (brick making jargon)	Unit weight of brick per given volume
SIA	Société Suisse des Ingénieurs et des Architectes / Schweizerischer Ingenieur- und Architektenverein. (http://www.sia.ch/f/index.cfm)
SIA Deklarationsraster	EPD for building products managed by SIA
STN	An online database service that provides global access to published research, journal literature, patents, structures, sequences, properties, and other data.
SWEDAC	Swedish Board for Accreditation and Conformity Assessment (http://www.swedac.se/sdd/System.nsf/(GUIview)/index.html
SWOT	An acronym for Strength, Weakness, Opportunities, Threats – An evaluation tool for for a project or a business in general that helps in identifying with a more or less systematic approach favorable and unfavorable internal and/or external factors influencing the outcome or result of the project or business.
Syngas	A gas mixture derived from gasification of coal and biomass or steam reforming of natural gas NG
TBE	Fédération Européenne des Fabricants de Tuiles et de Briques – Tile & Bricks of Europe, member association of CerameUnie (http://www.staywithclay.com/)
TEQ	Toxic equivalent (dioxin), measures all dioxins, furan and PCB's in reference to the most toxic 2,3,7,8-TCDD dioxin. TEQ is used to facilitate risk assessment and is sometimes applied by regulatory bodies to limit emissions.
Thermopor	Brick marketing organization in Germany and Austria representing about 20 single manufacturers (http://www.thermopor.de/)
TVOC	Total volatile organic compound
U – Value	A measure of air-to-air heat transmission (loss or gain) due to thermal conductance and the difference in indoor and outdoor temperatures. As the U-Value decreases, so does the qunatity of heat that is transferred through the glazing material. The lower the U-Value, the more restrictive the fenestration product is to heat transfer (reciprocal of the R value, $U = 1/R$) expressed in W/(K·m²)
UNI 8942	Prodotti di laterizio per Murature – Clay Brick Products (superseeded by EN 771.1 adopted in Italy as UNI EN 771.1)
UNIPOR	UNIPOR Ziegel Marketing GmbH (http://www.unipor.com/)
VELA	Italian brick manufacturer. (http://www.velaspa.it/index.php?option=com_docman&task=doc_details&gid=3&Itemid=56) VELA S.p.A.
Vertech	High temperature deep well oxidation process. See : Daun, M.; Birr, R. (1996) Klärschlammbehandlung durch Naßoxidation mittels VerTech - Tiefschachtverfahren.. In: Wasser und Boden, 48. pp 34-37
VitroArc	Fly ash vitrification process by EnviroArc
VOC	Volatile organic compound
VOG	Association of South Tyrolean Fruit Growers' Cooperatives – producer of apple based raw materials for the food and drink industry. (http://www.vog.it/)
VTT	Valtion Teknillinen Tutkimuskeskus - Technical Research Centre of Finland (http://www.vtt.fi/)
Web (brick making jargon)	Ceramic wall between two or more cores of a brick.
Wienerberger	Austrian brick manufacturer. (http://wienerberger.at)
Zipperle	Producer of fruit based raw materials for the food and drink industry. (http://www.zipperle.it/index.php?id=1&L=2) Hans Zipperle AG
- value	1. The quantity of air in the combustion process related to the volume needed. A value of 1 would indicate stoichiometric combustion 2. The rate at which heat is transmitted through a material, usually indicated in W/mK.

All above weblinks last accessed January 2010

Introduction

The main driver behind this work has been, as almost always the case in industry promoted research and development work, has been the desire to improve the the economic situation of a company.This thesis focuses on cored or hollow brick, a building material frequently used in continental Europe. It is about a nameless, imageless, no-brand product that is hidden behind a screen of plaster or paint most of times.

At the beginning of the research and development work in 1999 the Gasser brick company in South Tyrol was running substantial losses. The research and development work covers the following:

- Substitution of raw materials with waste materials;
- Substitution of fossil sources of thermal energy with alternative or renewable sources;
- Engineering of new firing systems and modifications to the tunnel kiln;
- Life Cycle Analysis to ISO standards;
- Novel and patented anaerobic biogas cascade fermentation system.

The results of the work, albeit having taken place in several distinct and well separated steps, have to be seen as an unique, integrated effort.The following chapters examine, in detail, the novel developments and technologies. Waste-based mixes are explained in Chapter 4 following page 93, energy questions are discussed in Chapter 5 following page 117 and Chapter 6 following page 131. Product related questions and product safety issues are dealt with in Appendix I following page 156 and in Appendix II following page 161.

At the conclusion of the work, this thesis sets the point of conclusion arbitrarily to 2006 when the results of the research and development work had become common practice at Gasser, the company had turned into one of the most profitable brick producers in Europe with the lowest environmental impact. Gasser has also been the first brick company in Europe to document and certify the change in the environmental impact of a brick production process due to fuel or raw materials changes by Life Cycle Analysis.

The prejudice that “environmentally friendly” is automatically associated with “expensive” has, in this case, been demonstrated to be incorrect : A large scale industrial production process can reduce its environmental footprint and at the same time become more profitable by reducing costs and opening up to new sources of income.

The work presented in this thesis details the steps and measures, and the underlying technical research and development work, spanning from material science to process technology, that the author researched, developed and implemented tat allowed to achieve these results together with the substantial and important reduction of the environmental impact of the production process and the associated products . Today, about a third of the raw materials entering the brick plant are wastes and the thermal energy required for the ceramic process comes from alternative and renewable sources. The change in the environmental impact of the production process is documented by Environmental Product Declarations (EPDs) and the financial impact by the income statements of the company. The achieved results are benchmarked either to the European or

Italian clay brick industry situation in general, see Appendix III, or to the pre-existing situation at the Gasser brick plant itself.

There is a significant amount of 'know-how' about recycling wastes into clay bricks, documented in many papers and research reports. Very little of this know-how has found its way into an industrial production process. An example for this might be the use of urban waste water treatment sewage sludge in brick making - known and documented since 1899 and, until recently[1], used on a regular basis only by three brick companies in the world. In general, the industry is focusing its research and development activity on improved web designs, reduction of density, optimization of the thermal conductivity of brick feeds and filling cores with insulation materials. The waste inclusion research and development work, contrary to the work concerning the application of alternative sources of energy, did not have to break completely new ground. However, one major limitation of most papers dealing with “waste incorporation” is that reported tests are usually only carried out at firing temperatures in the range of 900 °C to 1 100 °C. Another limitation is that the tests are normally carried out in electrically fired batch kilns. Cored bricks today are fired in tunnel kilns operated mostly with natural gas and generally in a temperature range of 750°C to about 950°C. Hence, even if the result of a reported waste inclusion test or trial in a brick feed looks promising, it still has to be investigated from first principles to verify its applicability to any intended production process. In the course of the research and development work a large number of wastes have been investigated and deemed to be unsuitable.

Of equal importance is a sensible use of process energy of which thermal energy constitutes by far the largest proportion. Energy sources used in the clay brick making process are predominantly derived from fossil fuels. However, through innovative development, it has been shown possible that these traditional sources can be successfully replaced by renewable alternatives, reducing use of fossil fuels and related greenhouse gas emissions to almost zero. Apart from some experiments with landfill gas, very little had ever been published about the use of alternative fuels in a brickyard. This work, in itself, is therefore both new and innovative. Some of the developments and applications of existing technology to the sector, for example the common rail fuel system featuring a common medium pressure single line fuel line with individual magnetic valves for each burner for example, have become common industry practice. The common rail biogas system is not yet common practice however.

The research and development work presented in this thesis began at the Ziegel Gasser Mattoni GmbH S.r.l. brickworks and has been carried out either under the direction and direct responsibility of the candidate or by himself personally. It has since expanded and been applied or further developed[2] to VELA S.p.A., Recuperi Industriali S.r.l. and Wienerberger S.p.A. in Italy and to SBBC Societè Briqueterie Bati Chaouia S.A. in Morocco. Further continuation of the work subject of this thesis is described following page 149.

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[1] VELA S.p.A. is using a waste materials based feed that does contain about 20% of digested sewage sludge.

[2] Two patents have been submitted but not yet published (April 2011)

Chapter 1

In the Beginning

1.1 The growth of commercial brick making in Europe

Is the study of brick making a study of civilization? Arguably, it might well be.

Fig. 1: Wall painting in the burial chamber of the Vizir Rekhmire in Thebes
18th DynastyEgypt (1550 - 1292 BCE)

Brick is the most ancient man-made building material and, without it, many cities would not have been built. Its durability makes it one of the most long term sustainable construction materials available.

The beginning of fired brick has been dated, by industrial archeologists, to about the third millennium BC (1)[1] in Çayönü, a place located in the upper Tigris area in south east Anatolia in Turkey close to the town of Diyarbakir[2] (2). The Egyptian pyramids were built with fired brick where straw had been added to the feedstock (3)[3] making them the first recorded example of a designed low density brick. Brick is the material that exemplifies the housing and much of the industrial history of our ancestors.. Although common,very few of its users know anything about the production process and the environmental implications of brick making. Unlike cars, for example, bricks are basically functional rather than items of widespread public interest – and, there are no fanzines[4]!

The actual term 'brick' is generally assumed to be a small, regularly shaped unit that a brick layer can grasp with one hand while picking up mortar with the other. Today, larger bricks/blocks, at least for cored bricks, are increasingly more common. However, it is still reasonable to describe these larger formats as being able to be handled and set by one person. For much of the long historic period of brick making, there was a more or less predictable demand and no great impetus to significantly improve production levels. Thus, the technology first adopted remained constant for a very considerable period of history. Almost without exception, where brick making was carried out, the bricks were routinely formed into shape by hand by filling appropriately sized wooden box-moulds

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[1] Except from a single finding dated about 5 000 – 4 000 BC in Maddur in Karnaka in India.

[2] In the cited book by Chandler a more comprehensive history of ceramics in general can be found.

[3] Makes reference to some early papers citing brick as well. The paper states that the same manufacturing method used by the ancient Egyptians is still in use today

[4] Not counting the various mostly technical publications such as Costruire in Laterizio, ZI – Ziegelindustrie International, Industria dei Laterizi, Brickyard Road etc. of very limited circulation. The United Manchester fanzine alone distributes about 10 times the copies sold by any of the aforementioned brick fanzines.

with a wet plastic clay mixture. The formed bricks were then carefully ‘turned-out’ and stacked, depending on the prevailing weather conditions, in the open or under cover to dry. Once sufficiently dry, they were then placed and fired in various types of basic intermittent kiln.

Brick is an universal product that comes in many regional different dimensional formats and shapes. This pattern of areal variability of specific brick sizes has continued to persist at a localized level and still continues, in a limited way, in many countries. In italy for example still exits a very strong market for “local” shapes and dimensions. In the US standardization of brick size began in the 1880s. The US National Brick Makers' Association adopted a standard brick size of 8 by 4 by 2 inches in 1887 and the US National Traders and Builders' Association in 1889 adopted standard sizes of $8^{1}/_{4}$ by 4 by $2^{1}/_{4}$ inches for common brick and $8^{3}/_{8}$ by $4^{1}/_{8}$ by $2^{1}/_{4}$ inches for facing bricks. These standards however, were not legally binding and brick dimensions continued to vary according to the whim of individual manufacturer and demand among their localized customers. In the United Kingdom the length and the width of the common brick has remained fairly constant over many centuries, but the depth has varied from about 2 inches or smaller in earlier times to about $2^{1}/_{2}$ inches in more recent times. The size of a modern metric brick in the United Kingdom is now 215 x 102.5 x 65 mm (about $8^{1}/_{2}$ x 4 x $2^{1}/_{2}$ inches). In German speaking Europe the size of the brick varied between 270 to 330 by 130 to 250 by 60 to 80 mm. In Austria in 1715, Emperor Karl VI ordered brick to be manufactured in the size of 11 by $5^{1}/_{4}$ by 2 $^{2}/_{3}$ “Austrian Zoll”[1]. These bricks are know as “emperor” size bricks. In Germany the first standard size brick was introduced by the Prussian Ministry for Trade, Trades and Public Works in 1872 and stayed in force until 1952. At the same time there also existed the so-called large and small Bavarian size bricks measuring 360 by 180 by 65 mm and 290 by 140 by 65 mm. In historical comparison the bricks used and manufactured in Babylonian measured approximately 350 by 350 by 90 mm and the Roman bricks varied in size between 600 by 600 by 100 to 200 by 200 by 20 mm. A complete and detailed overview of the European brick sizes and types around 1875 can be found in Kerl's book (4).

Today, brick making is still a relatively “regional” activity. No single “global” product exists. Brick making is still characterized by small operations. Even the largest, Wienerberger, has a turnover that is less than 15% of the turnover of Lafarge, the largest cement manufacturer[2].

In the early years of the 17th century a sudden spurt of industrialization occurred turning this “localized” (5), strictly artisanal and in many cases seasonal activity[3], into an industrial process with larger brick plant with permanent kilns. A comprehensive description of this transformation from local craft to industrial operation is given for example in a publication edited by the Municipality of Corte Franca (BS) in Italy (6), in a book by Hutton about the brick industry in the Great Hudson River Area (7) in the US and in a book by Kasberger and Eckard about the development of the town of Munich in Germany and

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[1] 1 Austrian Zoll (inch) = 2.63 cm. Metric dimensions 28.93 x 13.80 x 9 cm.

[2] Reference 2008

[3] The book edited by Badstüber and Schumann collects a number of papers by various authors covering the subject of middle age and later periods brick making and usage in Germany and Italy.

the brick industry that allowed and contributed building it (8). These are just a few examples. The industrial production of brick was also origin, as narrated in (8), of seasonal immigration: Thousands of workers flocked from Northern Italy every year until the late 19th century, to work in the brick plants of the "Loambarone", the Clay Barons, at the outskirts of the city of Munich.

Industrial development in brick making was fueled by a sharp increase in the expansion of urban dwelling that required a steadier, large volume, flow of building materials all year round to satisfy the housing needs. This unprecedented demand for brick turned the long established traditional brick making practices into a high-output commercially driven enterprises. Accompanying this impetus came a vast array of newly invented production machinery and equipment to mechanize different steps of the overall brick manufacturing process. This technological advancement did not always occur in parallel in all European countries: Different market situations, environment conditions and clay types led to different types of machines and divergent processing techniques. These innovations affected all three of the basic brick making steps i.e. forming, drying and firing. Quarry activities also became increasingly less dependent on manual labor as they turned to mechanical means of winning and transporting clay.

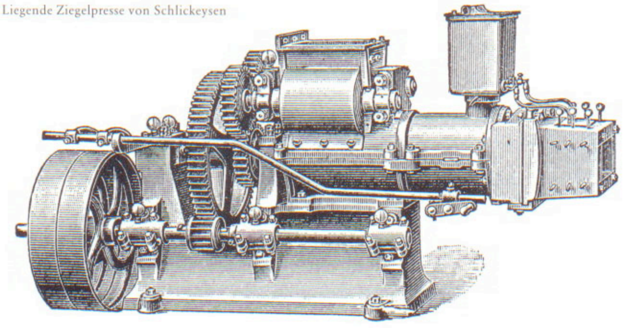
The following examples of important steps stand as milestones in the broad pattern of progress and increased productivity that has led to today's highly mechanized brick manufacturing sector (9) (10) (11).

Table 1: Recognized major steps in the progress towards modern-day brick manufacture

1619	1810	1840	1854	1858	1873	1877	1894	1906	1910
Etherington manual piston extruder	Kinsley soft mud moulding machine	Yord tunnel kiln [1]	Schlickeysen horizontal extruder	Hoffmann kiln	Bock tunnel kiln	Tunnel kiln sand seal by Brunswick	Keller dryer	Haendle box feeder	Keller automatic cutting and setting machine

The rate at which bricks could be formed was greatly advanced by an invention by Carl Schlickeysen in 1854. This consisted of introducing a vertical continuous worm or screw running inside a steel tube (12) (13) through which plastic clay could be fed and forced out to produce a plastic oblong column of variable dimensions, which could then be cut into individual bricks. He later improved on this design by having the unit extrude in the horizontal plane as pictured below.

Fig. 2: Schlickeysen horizontal extruder



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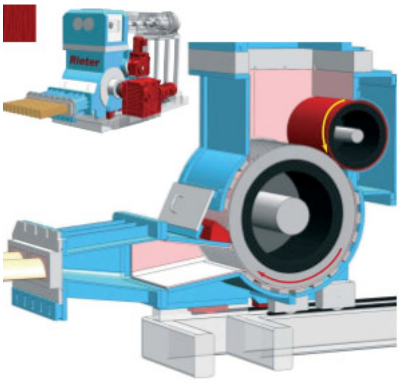
[1] Albeit there are tunnel kilns documented as early as 1760.

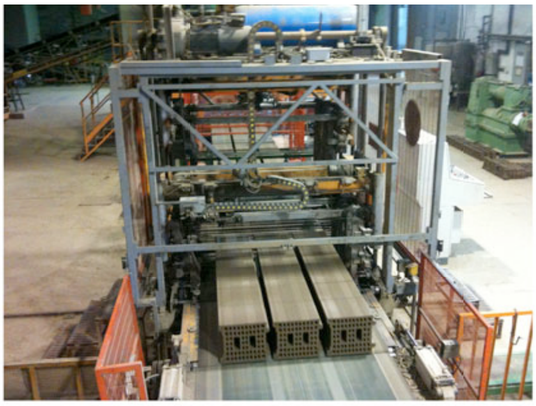
Modern extruders, except for the Rieter Konstanz horizontal rotor “Euro Press”, have grown larger in size and usually feature a de-airing chamber but are still based on the same principle as the Schlickeysen extruder.

Fig. 3: Rieter horizontal rotor extruder[1]



In 1910 Carl Keller built the first automatic device for cutting the freshly extruded clay column into the desired length and a setting machine for green bricks.

Fig. 4: Modern multiple wire cutter for multiple strand extrusion



Another machine without which modern brick making would be almost impossible is the box feeder. The first continuous box feeders were built in 1906 by Händle for which a patent (14) had been obtained.

Fig. 5: Original Händle 1906 box feeder[2]

Before that, manual feeding was required.

A modern box feeder does not differ substantially from the 1906 model:

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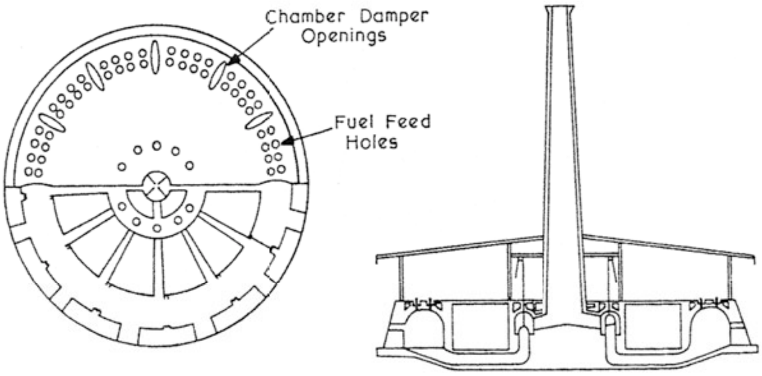
[1] Taken from company brochure.

[2] Taken from a paper by Bender published in ZI Ziegelindustrie in 2006.

Fig. 6: Händle box feeders in a modern brick plant around 1985

In 1854 Friedrich Hoffmann, together with Albert Licht, obtained a first patent for a new kiln for the continuous firing of bricks. The first kiln of the new design was built in Scholvin near Danzig in Germany. A "biography" of the Hoffmann kiln has been published by Schiya (15) including a facsimile of the original Prussian Hoffmann patent. A comprehensive overview of kiln and firing technology development can be found in Schiya (16) and in Rauls[1] (17). The latter is a comprehensive overview of the state of the art in continental Europe at the beginning of the 20th century. The Musèe des Arts et Métiers in Paris has a wooden model of the Hoffmann kiln in its permanent exhibition.

Fig. 7: Original circular Hoffmann kiln (plan, elevation and section of 12 chamber unit)



The Hoffmann (6) (7) (8) kiln is made up of a number of chambers, which are fired sequentially one after the other - the fuel being fed in through fire-holes in the roof of each chamber at the appropriate time. After the fire-zone has passed, the bricks in the newly fired chambers are left to cool down. When cool enough, they are removed and the chambers they occupied re-set with fresh, unfired bricks waiting their turn to be fired. An ingenious system of air-ducts allows the most recently fired bricks to impart their cooling heat into a flow of air that was directed around them and this was conveyed forward into the sector of chambers that had just been set with fresh unfired bricks allowing them to heat up in preparation for firing. The fire-front moved in a constant direction around the chambers, thus permitting the kiln to burn continuously without interruption. This was a continuous process i.e. it went on non-stop and achieved a significant reduction of overall energy requirement compared with the earlier types of intermittent kilns. Around 1900, more than 4,000 Hoffmann kilns have been in operation around the world (18). It is one

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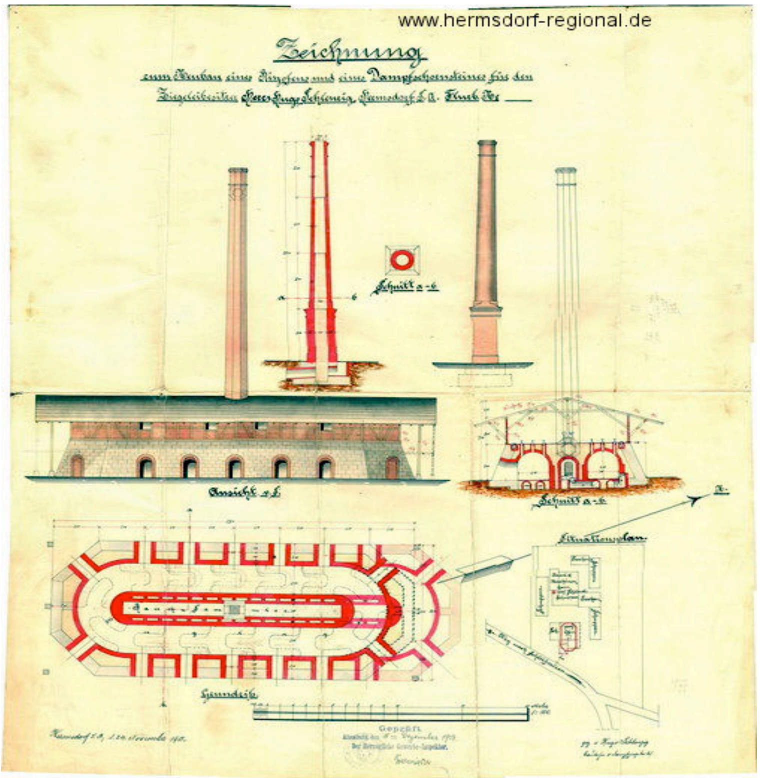
[1] Franz Rauls was a German engineer who designed and built a number of brick works as far as Brazil and published both technical, dealing mostly with clay ware, and fiction books

of the most successful brick kiln designs achieved and continues to be used, albeit on ever more limited scale, worldwide (with minor local changes).

The design was originally circular in form but later, to save space, was modified to a rectangular or oval shape.

Fig. 8: The later oval Hoffmann kiln (plan, elevation and section)
(Ziegelei Hermsdorf - Germany)



The main advantage of the Hoffmann kiln was its fuel saving: over 70% when compared to previous designs. Many Hoffmann like kilns are still in use around the world.

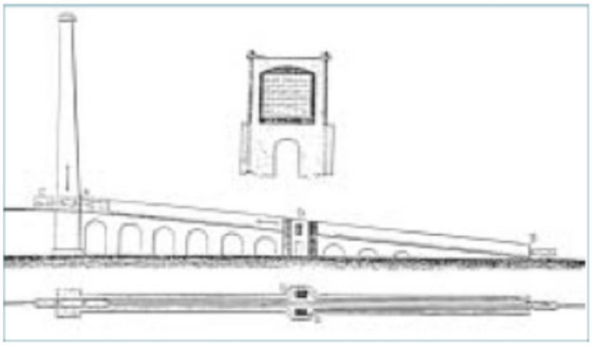
Fig. 9: Fired brick ready to be drawn inside a firing chamber of a
Hoffmann kiln in a brick plant in Colombia (2009)

A number of kilns based on Hoffman's original patent, with the provision of a multiplicity of movable iron dampers for controlling the flows of cold intake air, and hot exhaust gases, allowing maximum thermal efficiency, have been built or patented later for example by De Witt (19) (20) (21) (22) (23) and in the US with moveable stacks by Rhodes (24).

Another form of continuously operating kiln destined to have a far reaching impact on the growth of commercial brick manufacture, is the tunnel kiln. The first patent has been obtained by York in Flensburg[1] in 1840. The kiln, the first one was built in the Katharinenhof brick plant, did not deliver the desired results and was demolished after only two years of unsuccessful operation in 1848[2]. The main advantage of the tunnel kiln over a Hoffmann kiln is that the tunnel kiln allows for relatively simple mechanical handling, loading and unloading of the kiln cars. Böger describes the history of firing bricks in tunnel kilns in great detail in his ZI Ziegelindustrie International paper (25).

A very interesting variation of the tunnel kiln idea is the inclined tunnel designed by Borrie in 1855.

Fig. 10: Borrie kiln – schematic drawing

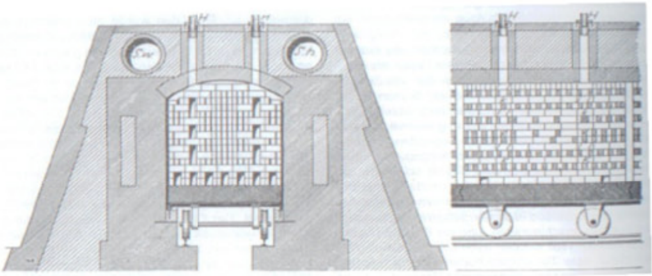


The kiln cars are fed at the higher end of the tunnel and travel, by gravity, to the lower end. From the literature examined it is unclear if such a kiln has ever been built or operated.

In the tunnel kiln, packs of bricks set on a car train on rails move through the kiln one after the other. During their journey, the cars move towards, through and past the stationary firing section at the center of the structure. During its travel the brick set on the kiln car is slowly heated up to the desired firing temperature and then cooled down again.

The first practical and working design for a tunnel kiln in the ceramic industry was produced by Otto Bock (10) in Braunschweig, Germany.

Fig. 11: Section and car profile of Otto Brock's tunnel kiln fitted with a sand seal



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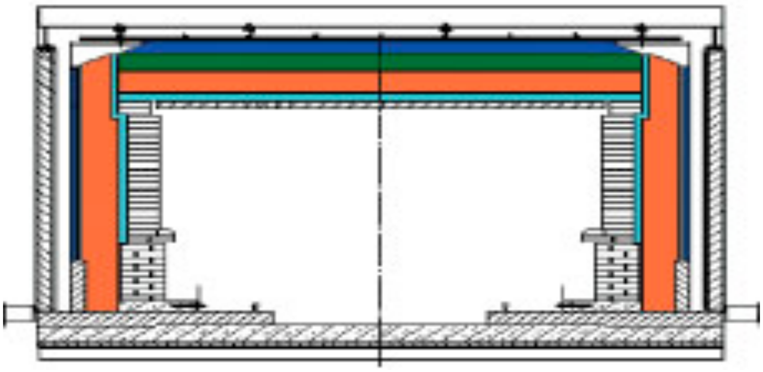
[1] The then Danish town of Flensburg became German in 1964.

[2] In 1880, 40 years after York obtained his patent, Foster built a 2.5 x 3.3 x 33 meters tunnel kiln in Yorkshire.

In 1877 a German Imperial Patent (No. 1340) was granted. This design incorporated a sand seal - this system[3] is still in use today in almost all tunnel kilns - which isolated the under-carriage of the cars from the hot gases circulating in the kiln. The tunnel kiln became widely accepted only after 1947 (26). The Bock kiln can be considered to be the first modern tunnel kiln. Another method for insulating the kiln car underbody from the hot gases was running the kiln cars under-carriage submerged in water right below the level of setting of the bricks. These "hydrocasing" kilns have been developed and built by Ceric (27). Most of these kilns have however been converted to dry operation due to corrosion problems to the undercarriage of the kiln cars.

A modern tunnel kiln, as the one pictured following, does not differ, except for the use of better materials, from the Bock kiln pictured above. The kiln side walls are not any more solid but light weight constructions and the ceiling is not any more vaulted but rather suspended from the load bearing structure. Most modern tunnel kilns also do not have any more the possibility of access from underneath during operation by means of an access tunnel.

Fig. 12: Section of Keller HCW tunnel kiln



Very soon a major shortcoming of the tunnel kiln, the poor circulation of the hot gases around the brick stacked on the kiln cars and hence poor heat transfer rates, became apparent.

A purpose built recirculation system is mentioned in the 1920 patent of Francart (28). This patent is based on a prior patent granted in the UK in 1918. Metcalfe, in his patent[2] (29), as well felt the need of better distributing the hot combustion gases, generated in combustion chambers located outside of the kiln, around the bricks to be fired. Recirculating and alternating gas flows are the subject of a patent by Packham and Ball of 1905 (30) and of Haessler in 1981 (31). Heat recovery has been an issue in 1907 for Oxley and Crossley (32).

Except from a few roller kilns, these type of kiln however did not find a market in the cored clay brick business, no major new developments are on the market: Bricks are still fired tightly packed on heavy kiln cars (Figure 13 below).

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[3] The sand seal apparently has been, without the inventors having knowledge of each other, invented at around the same time both in Germany and the US.

[2] Only the German patent is accessible as document albeit the invention appears to have been patented in the US and the UK as well.

Fig. 13: Bricks on a kiln car in a modern plant
(VELA S.p.A. Fornaciai Bologna)

The tight packing of the bricks is a great impediment to good firing as most of the bricks in the inner layers reach their firing temperature with a substantial delay compared to the outer layers. Some kiln manufacturers today favor a design with a lower stacking height of the brick on the kiln car in order to ease circulation of hot gases around the brick.

The introduction and extensive use of tunnel kilns has not been equally rapid throughout the brick industry: In 1968, for example, 53% of the Austrian brick plant had already commissioned tunnel kilns, whilst in the UK over the same period this figure was as low as 8% (26) when calculated on total number of installations.

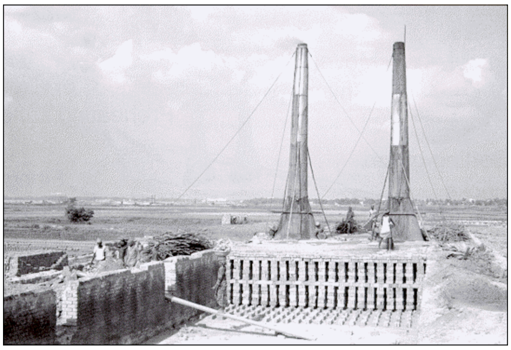
In developing countries clamp and trench kilns are in wides use. Clamp kilns can be fired with a wide choice of solid fuels, from coal to wood to dried dung, available locally.

Fig. 14: Clamp kiln (Africa)

The kiln is, once the bricks to be fired are properly set, covered with earth and then fired.

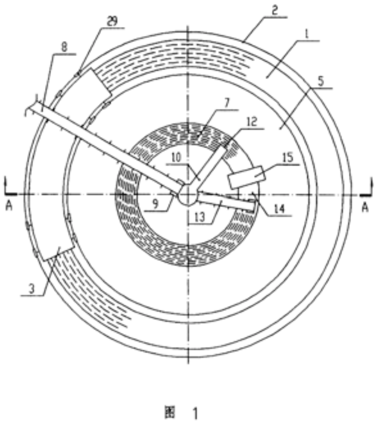
Shortly before 1900 the British engineer Bull developed the oval shaped trench kiln. It is widely used all over Asia. A trench kiln is easy and cheap to built. Operation of a trench kiln is continuous.

Fig. 15: Trench kiln (Pakistan)



A curiosity is the circular kiln developed and patented in China (33), a kiln in which the material to be fired is fixed and it is the fire that is traveling.

Fig. 16: Circular track kiln with mobile firing chamber (China)
(from the original Patent)

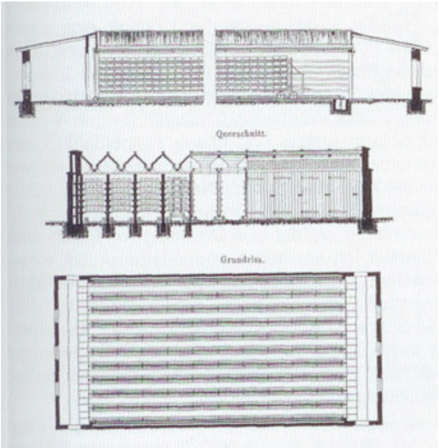


On a circular track elevated from the ground level (2 in the above drawing) bricks are set to dry and later fire. The circular firing chamber travels and the bricks in the firing chamber are fired. Apparently, extraction fans are installed underneath the track. No indication about the fuels used is given. A kiln of this type appears to have been built but no definite information, except the patent, has been obtained.

In addition, Rauls (17), Clews (54) and Searle (41) depict many more interesting types of kiln. None of them has gained however such a paramount importance as the Hoffmann and the tunnel kiln.

Notwithstanding the success of the technical advances in forming and firing bricks in the 19th century, one major production problem still persisted for a considerable time and as a consequence, continued to handicap even greater levels of productivity. This issue was concerned with how to speed up the brick drying process to match the rate that these products could now be produced and fired. Previously, this essential pre-firing operation had relied on the bricks being dried , sometimes under cover, outside in the brickyards - and therefore subject to unpredictable weather conditions.

Fig. 17: Keller dryer



However, in 1894 Carl Keller constructed an experimental chamber dryer in combination with finger-cars. As a heat source he used finned tubular heating pipes supplied with waste steam, live steam or hot water. Nevertheless, difficulties arose in the removal of the moisture-saturated air surrounding the bricks, with the only exit route being via natural venting through roof slots in the chamber, a suction channel and final discharge stack. There was very little means of optimizing the performance of this equipment, because the natural draught of the exhaust stacks was dependent on the outside ambient air conditions that were frequently changing.

The later introduction of artificially induced draught controlled by automatic regulation brought freedom from the earlier dependence on natural draught. Jacob Bührer, see (10) for more information, built the first recorded commercial chamber dryer in his father's brick plant where he obtained drying heat by means of a suction fan (driven by a water wheel) from the kiln off-gases.

Fig. 18: Jacob Bührer advertises his engineering services [in (17)]

JAKOB BÜHRER

KONSTANZ (DEUTSCHLAND)

ZIEGELEITECHNISCHES BÜRO / KOMM.-GES.

GEGRÜNDET 1860 / EIGENE PATENTE

Ältestes Konstruktionsbüro

für den Bau vollständiger

Ziegelei-Anlagen

nach eigenem System, Zickzack- und Langöfen mit Ventilator- und Kaminzug.

Kammer-, Kanal-, Gang- u. Gebäude-Trocknereien

mit automatischer Beschickung und Entleerung, für die Trocknung selbst des empfindlichsten Rohmaterials, sowie aller Warengattungen, vorzüglich geeignet. Trockenanlagen mit **Feuchtluftanwendung.**

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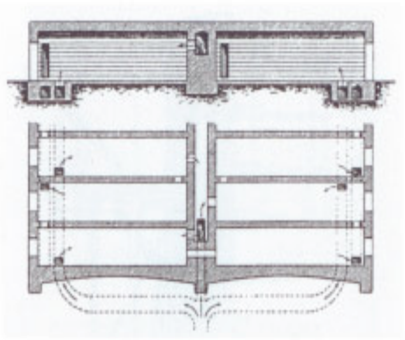
Bührer obtained two patents for his dryers (34)(35). The first large-scale plant using his system was built at the Münchner Aktienziegelei brick-works, at this time one of the largest brick producers in the then German Empire (36). This plant consisted of a longitudinal zigzag kiln (also developed by him - such kilns are still in use in the Far East as, for example, in Bangladesh (37)(10) equipped with a suction fan that removed flue-gases from the kiln exhaust to be passed to the dryer. Around 1870, a drying plant with heating via kiln waste heat was built by Hoffmann. This can be considered as the predecessor of the channel (or tunnel) dryer (38) (Figure 18). A mobile base (car) with six tiers was stacked with the freshly made bricks which were driven into short chambers situated next to one another. Shortly after this a true tunnel dryer was developed by Buhler in Uzwil, Switzerland. They also appeared in England and North America at about the same time (4).

Fig. 19: Plan and cross section of a Hoffmann dryer



The conclusion of this brief history of brick making machinery might be left to Bender (39). He states "*On closer consideration, however, it is clear that all the persons mentioned are not original inventors in the sense that they had created a technical innovation, for which there were no archetypes to date. Instead it is common to all of them that they have taken up already existing ideas or designs, but helped them to their functional maturity and general market introduction through decisive improvements, constructional innovations and personal effort".*

1.2 Brief overview of the stages of brick manufacture

As background ahead of describing the research and development work in detail, it is beneficial to briefly review the various processing steps that bricks undergo before they become a final finished product. The slow adoption of new technologies becomes notable when comparing brick making handbooks such as the one Bender & Händle (40) published in 1985. Searle published 4 editions of this book between 1891 and 1956 (41)[1]. Avenhaus, in his short book (42), looks at brick making from a more practical point of view as did Clews and Green (43) in their book from1969.

Brick manufacture is usually subdivided into a number of definable steps as set out in Table 2 .

Table 2: Overview production methods bricks

Winning and storage of raw materials (44)	In the clay industry, winning and storage of raw materials follows usually open cast mining procedures. Surface clays, shales and some fire clays are mined in open pits with power equipment. The mixtures are then transported to plant storage areas. Winning and storage might also include the utilization of waste or secondary raw materials in the body. It is common practice to store enough raw material for several days' operations, thus ensuring continuous operation regardless of weather conditions. Normally, several storage areas (one for each source) are provided to permit some blending of the clays. Blending produces more uniform raw materials, helps to control color and permits some control over raw material suitability for manufacturing a given type of product.

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[1] 4th edition, last in the series, in 1956

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Preparing raw materials (44)

Usually preparation includes aging, cleaning, crushing, grinding, screening, proportioning, mixing and wetting. Winning and storage and preparing sometimes overlap depending on work flow organization in the quarry and the plant itself.

↓

Forming units (44)

The first step in the forming process, produces a homogeneous, plastic mass ready for molding. It is most commonly achieved by adding water to the clay in a pug mill, a mixing chamber which contains one or more revolving shafts with blades. After pugging, the now plastic clay mass is ready to go to the forming step. When the wet clay units come from molding and cutting, they contain, depending upon the forming method, between 5 to 30 percent moisture.

Soft Mud Process	Stiff Mud Process	Dry Press Process
Mostly used for cored and hollow brick	Mostly used for facing brick	Very uncommon process for all types of brick
The soft-mud process is particularly for clays which contain 15 to 25 % (or even more) of water by weight.	In the stiff-mud process, clay is mixed with only sufficient water to produce plasticity, usually from 12 to 15 percent by weight.	This process is particularly adaptable for clays of very low plasticity.
After thorough mixing, i.e., "pugging", the tempered clay goes through a de-airing chamber in which a vacuum is maintained. De-airing removes air holes and bubbles, giving the clay increased workability and plasticity, thus resulting in greater strength. Next, the clay is extruded through a die to produce a column of clay in which two dimensions of the final unit are determined. The column then passes through an automatic cutter to make the final dimension of the brick unit. Cutter-wire spacings and die sizes must be carefully calculated to compensate for normal shrinkage during wet stages through drying and firing (see Size Variation).		Clay is mixed with a minimum of water (up to 10 percent), then formed in steel molds hydraulic or compressed air rams.
	As the clay column leaves the die, textures or surface coatings may be applied.	

↓

Drying (45) (46)

Rapid dryers today dry a hollow brick in 3 hours or less. Standard continuous or chamber dryers require, depending on design of the dryer and the type of brick to be dried, between 18 and 45 hours. The moisture content of a brick drops from the percentage present at extrusion to a value of between 1 and 5% usually. In modern plants after the process of drying the bricks are automatically repackaged into a firing setting and automatically transferred to the kiln by kiln cars. If periodic kilns are used, transfer from the drying station might be manual. In a Hoffmann type kiln the bricks are stacked wet.

Roof or floor tiles are sometimes tried by combined infrared or microwave processes. It has been tried, without success, to implement such a drying process also in the cored clay brick industry but with no success until now.

↓

Firing (47) (48) (49)

Firing and cooling, one of the most specialized steps in the manufacture of brick, requires, depending on the technology used, usually from 4 to 30 hours for continuously operating tunnel kilns and between 15 and 150 hours, in some very rare cases, in periodic kiln.

↓

Drawing and storing finished

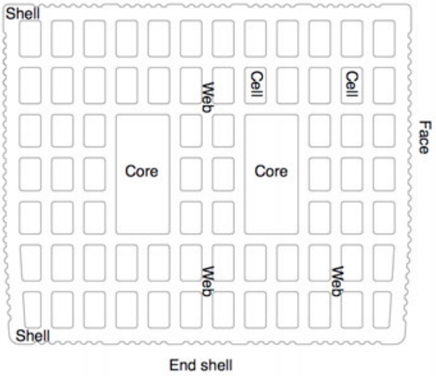
At the end of the firing stage that units are sorted, graded, packaged and taken to a storage yard or loaded onto rail cars or trucks for delivery. The majority of brick today are packaged in self-con-

products	tained, wrapped or strapped cubes sometimes placed on pallets for easier handling with cranes or forklifts.

1.3 The evolution of different brick sizes and configurations

The outer frame of the brick is usually defined as the shell whereas the internal division bars between cells and cores are referred to as webs. The passing cavities are either defined as cells (when smaller) or cores (when larger).

Fig. 20: Terminology



The total area of the cores and cells is defined as the percentage of voids. A full brick usually does not have a percentage of voids of more than 20% of the total surface of the brick while a cored brick has less than 45% of voids. A hollow brick will have up to 65%, or even more, of area of voids. The side of the brick exposed to the view or to the rendering is defined as face. The side connecting one brick to the other is the end shell.

Local custom, tradition and diversification of shapes and sizes to achieve desired product characteristics has lead to a proliferation of clay building products (see Figure 20 below for a few examples), a large manufacturer like Vela S.pA. in Italy lists more than 70 products in its catalogue.

Fig. 21: Load bearing and non load bearing cored and hollow clay bricks and blocks manufactured in some European countries

ThermoPlan® S 9
(machined block)
JUWÖ, Germany

ThermoPlan® TS 13
(machined block)
Rimmele, Germany

Dividers
Venus, Germany

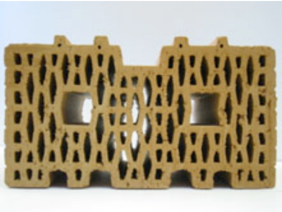
PLANZIEGEL PD 0,12
(machined block)
Hüning, Germany

Pignatte 12x25x42
Wienerberger Italy

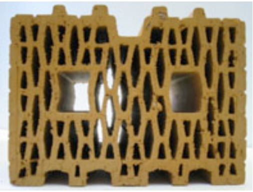
Alveolater 45
Laterizi SIL, Italy

Mattone 21 Fori
Archina, Italy

Tramezze “12”
Vela S.p.A., Italy



Blocco 42 (obsolete design)
Gasser, Italy



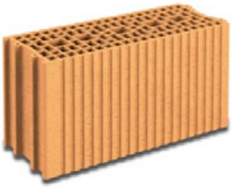
Blocco 38 cm (obsolete design)
Gasser, Italy

Blocco 38 cm λ 0.14 (new design)
Gasser, Italy

Eco'Bric
Bouyer Leroux, France

Thermo'Bric
Bouyer Leroux, France

MONOMUR 37,5 JOINT MINCE
Imerys, France



MURBRIC T20
Wienerberger, France

Ladrillo cerámico hueco portante
Ceramica Garcia, Spain

Termoarcilla
Fantini Scianatico, Spain

The writing of the European Standard EN 771-1 for the entire and complete clay product family [i.e. load bearing or non load bearing cored or hollow bricks, blocks, wall tiles, lintels etc. (50)] has to recognize differences in traditional construction influencing the type and size of individual brick products in response to the climates that prevail (which vary from almost Arctic to Mediterranean) and local demand and customs. In some EC Member States, for example, in the United Kingdom, Belgium and the Netherlands, almost no hollow load bearing clay blocks are manufactured, but rather smaller cored and solid bricks.

In Italy, large module hollow blocks of the type shown above are the main product used and manufactured. Yet this large-block format has itself undergone an on-going evolutionary process since its earliest inception.

The characteristics of brick, mainly density and hence thermal resistance, have changed substantially over the years. Thus, the number of cores has been increased, the thickness of the webs and outer walls decreased and material density has also been reduced. This is mainly due to the widespread use of organic additions, many times addressed in literature as pore forming agents, to the brick body, that are commonly included during their manufacture that burn-out during the firing process leaving small cavities within the brick body.

Table 3: Evolution of characteristics of Thermopor bricks (since about 1982 machined)[1]

	Wall thickness in mm	Apparent density kg/l	Mechanical resistance class DIN 105	λ_{brick} value in W/mK
1977	240, 300, 365, 490	0.73 – 0.81		0.21 – 0.31
1995	240, 300, 365, 490	0.80	6 – 8 - 12	0.16
2005	240, 300, 365, 400, 425, 490	0.55	4 – 6 - 8	0.09
2008	300, 365, 400, 425, 490	0.60	4 -12	0.08

From 1977 to 2008, the thermal performance of brick has improved considerably.

Another improvement, a product that has become popular mainly in the German language countries and is now slowly spreading to the rest of Europe, is the machined or planed brick. This has been first manufactured by Oltmanns, now owned by the Wienerberger group, around 1980. The cored surface of the brick are mechanically planed to be perfectly parallel and all bricks are of exactly the same height in order to allow for mortarless masonry, i.e. no hydraulic or hydratic binder based mortar needs to be used in between the joints improving thermal and acoustic characteristics.

Fig. 22: Setting example of mortar less load bearing brick wall with machined or planed brick[2]

Lately bricks with insulation material filled cores have gained some popularity in Germany and neighboring countries. The cavities of these bricks are filled with insulation materials to improve on thermal characteristics. The rockwool filled UNIPOR Coriso (Figure 22 center) and the “Mein Ziegelhaus” (Figure 22 right) brick as well as the one developed by Schlagmann (Figure 22 left) and filled with expanded perlite, all feature an U value of ≈ 0,08 W/mK . The manufacturing cost of these bricks is, due to the cost of the filling material itself and the process of filling the voids, high when compared to a standard brick and hence command a far higher selling price.

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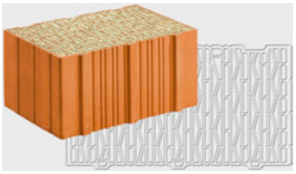
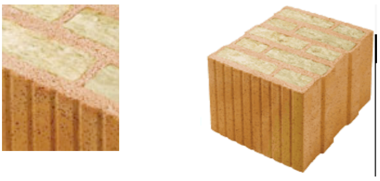
[1] Company data. Catalogues and advertised data. For 1972 unpublished data IZF – Institut für Ziegelforschung Essen

[2] A planed or machined brick is a brick that after firing is mechanical machined to an exact height and perfect planarity. The first brick maker to market such brick has the been the German company Oltmann (today Wienerberger).

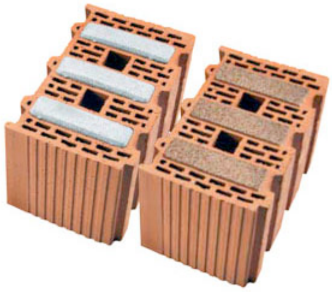
Fig. 23: Examples of brick with filled cavities (51) (52) (53)

Schlagmann	UNIPOR CORISO	Mein Ziegelhaus
		
Design introduced in 2002 (first manufactured in 1998 with different web design). Perlite filled	Introduced in 2007 Rockwool filled	Introduced in 2008 Rockwool filled

The difference between the two rockwool filled bricks is, that the CORISO UNIPOR brick has a filigree web structure (Figure 22 above left) whereas the Mein Ziegelhaus brick (Figure 22 above right) strongly resembles the earlier introduced Schlagmann brick with thick webs and walls but differs for the material used in filling the cores. The material density of these bricks is in the range of 1.25 kg/l to about 1.45 kg/l depending on manufacturer and type.

Issues such as dew point localized at the contact surface of the filling with the brick and hence a risk that the filling will become soaked, due to the humidity transport characteristics of the brick itself, are not addressed at the moment by the manufacturers of these bricks. This soaking would result in a partial or total loss of its insulation properties. A further risk not addressed is fire in case the filling is made with combustible materials such as polystyrene.

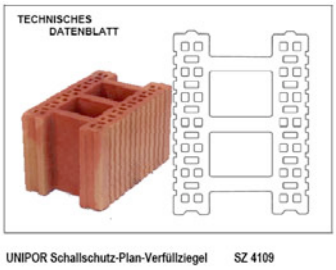
Fig. 24: Example of brick with polystyrene and natural cork filled cavities manufactured by Latertech in Italy



The Italian brick claims thermal insulation values similar to the ones of the German bricks pictured above. The Italians claim their values always for rendered brick whereas the values for the German brick are for the wall alone. Hence the Italian brick is intrinsically of lesser thermal performance. Another major difference is the much higher material density, > 1,55 kg/l, and the webs and shells being wider than the northern European counter part [see (54) for a complete overview of insulation material filled bricks].

Special shaped bricks, such as the one pictured below with cavities to be filled with concrete, are also becoming popular for special applications such as sound insulation or fire walls.

Fig. 25: Example of high void percentage clay products with concrete core-filling (Rimmele Germany)



Novel applications of standard brick include, for example, shaped (Figure 25 below) brick structures.

Fig. 26: Shaped brick structures

In the future one of the major issues for the brick industry will be the thermal mass (heat capacity or thermal capacitance) regulation of the building envelope, outer walls, and its effect on the energy performance of buildings (55) . A higher thermal mass results in a better damping factor (56), especially important in climates with substantial variations in temperature during the day. Italian legislation calls for a minimum mass of 230 kg/m^2 of wall (57). Austrian standards require all new buildings to feature a minimum thermal capacitance of the wall (58) without specifying an unit weight [see (59) for some example calculations]. Lightweight constructions often exhibit an insufficient damping factor and often suffer from summer overheating that requires a great expense for cooling in order not to be inhabitable (60). Standards such as ISO 13790[1], applicable to new and existing buildings, will provide a more accurate energy balance of the building considering summer air-conditioning systems, hot water production and lighting as well.

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[1] ISO 13790 gives calculation methods for assessment of the annual energy use for space heating and cooling of a residential or a non-residential building, or a part of it, referred to as “the building”.
This method includes the calculation of:

- The heat transfer by transmission and ventilation of the building zone when heated or cooled to constant internal temperature;
- The contribution of internal and solar heat gains to the building heat balance;
- The annual energy needs for heating and cooling, to maintain the specified set-point temperatures in the building – latent heat not included;
- The annual energy use for heating and cooling of the building, using input from the relevant system standards referred to in ISO 13790:2008 and specified in Annex A.

ISO 13790 also gives an alternative simple hourly method, using hourly user schedules (such as temperature set-points, ventilation modes or operation schedules of movable solar shading).
Procedures are given for the use of more detailed simulation methods to ensure compatibility and consistency between the application and results of the different types of method. ISO 13790:2008 provides, for instance, common rules for the boundary conditions and physical input data irrespective of the calculation approach chosen.
ISO 13790 has been developed for buildings that are, or are assumed to be, heated and/or cooled for thermal comfort of people, but can be used for other types of building or other types of use (e.g. industrial, agricultural, swimming pool), as long as appropriate input data are chosen and the impact of special physical conditions on the accuracy is taken into consideration.
The calculation procedures in ISO 13790:2008 are restricted to sensible heating and cooling. The energy use due to humidification is calculated in the relevant standard on the energy performance of ventilation systems, as specified in Annex A; similarly, the energy use due to dehumidification is calculated in the relevant standard on the energy performance of space cooling systems, as specified in Annex A of the ISO standard.

1.4 The evolution of brick making raw materials

Keramikos and Keramos: The first term defines a trade, pottery hence the art of mixing clay and water, the second the specific raw material, potters clay or the mixture of water and clay, needed for this trade. The term “ceramic raw materials” defines any inorganic, nonmetallic material that can be shaped and fired. The term includes, but is not limited to, clay in the classic sense. Brick manufacturing is still tied very much to raw materials in the classical sense of the word “Keramos”.

From a scientific point of view, the raw materials used in brick making are decomposition products of feldspar-rich rocks. Depending on origin and ratio of decomposition, the spectrum of clays ranges from kaolin to sandy loams. The raw material in the quarry usually consists of a mix of clay minerals, rock residues and materials that resist decomposition due to weathering such as quartz.

Clay minerals form plate shaped crystals or agglomerates who’s surface is generally greater than their thickness: SiO_4 tetrad and $Al(O,OH)_6$ octal layers are bound within this structure. Clay minerals with one tetrad and one octal layer are defined as two layer minerals, whereas in three layer minerals the octal layer is disposed symmetrically between two tetrad layers.

The SiO^{4+} cation can be exchanged for a lesser charged Al^{3+}cation. Al^{3+} can be exchanged for a Mg^{2+} cation. Either alkali or alkaline earth metals can compensate the missing positive charge. Introduction of alkali ions in the silicate structure weakens the bond. This is the reason why sodium and potassium ions act as sintering, temperature-reducing fluxes.

The most important raw materials in brick making are kaolinite and the minerals of the montmorillonite, illite, mica and chlorite groups that come in many forms and substitutions. These act as the main plasticizing component in association with water.

The quarried materials further contain decomposed feldspar. These components are defined usually as *grogs*.

Dolomite, calcite and ferrous substances, in the form of hydroxides, oxides, sulfur-rich pyrite or marcasite, are also found.

The characteristic physical properties of clay include plasticity which when wet, has the ability to form colloidal suspensions when dispersed in water and the tendency to agglomerate together (flocculate) and settle out in saline water. A good brick clay should have low shrinkage and low swelling characteristics, consistent firing color and a relatively lowfiring temperature, but, at the same time, produce an adequate dry and fired strength. In compositional terms, it should possess a low limited percentage of carbonate minerals, a small percentage of lime and a sufficient percentage of hydrated aluminum silicates (clay minerals). If the brick is to be red burning, iron oxide (the chief colorant responsible) should be ideally in the range 5 -12% (for good strong color)[1].

From a practical brick maker's viewpoint the assessment of suitability of a given brick clay depends upon the following characteristics:

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[1] Under oxidizing firing conditions in the kiln.

- A high percentage of larger particles requires higher sintering temperatures resulting in a greater energy requirement and longer firing times;
- Accessory minerals like Quartz, Feldspar and Amphibole have an effect on the sintering behavior and might result in undesired colors;
- Organics create voids in the finished product. If the organics feature a high sulfur content this might have effects on color, the fumes and the kiln atmosphere;
- Minerals such as Pyrite and Marcasite release SO_x on firing creating large diameter pores in the brick that might reduce compressive and flexural strength;
- Calcite, dolomite and other carbonate minerals such as, for example, Ankerite and Siderite, do have, if finely dispersed, a positive effect on the release of low temperature carbonization gases due to formation of channels and funnels but will reduce in larger quantities the compressive and flexural strength of the final product and might lead to chipping on the surface;
- A low earth alkali content, Magnesium and Calcium being the most common, is desirable to avoid firing interactions which could promote discoloration of the final product.
- Goethtite and Hematite, for example, both metal oxides and hydroxides and both containing iron oxide (the chief colorant responsible) that should be ideally in the range 5 - 12% (for good strong color), are the main origin for the red brick color;
- Natural radioactivity of the raw materials (radon).

Clays that are “strong” or plastic such as ball clays, are known as fatty clays, and always contain a significant high percentage of clay minerals and a low percentage of accompanying non-plastic minerals such as, for example, silica. Such clays take up a considerable volume of water, characteristically dry slowly, shrink greatly, and so frequently become liable to distortion and develop cracks in drying and firing. Historically, such fatty clays are greatly improved by the addition of sand (SiO_2) that acts as a filler to give rigidity and counteract distortion that reduces the time required for drying and also modifies shrinkage behavior during drying and firing. Sand together with straw are historically the first addition widely used in brick manufacture. They illustrate the broad function of “addition improvement” – a concept which has now been greatly expanded with the use of wastes.

Traditional brick manufacturing is normally restricted to common clays, shales and marls, but sometimes fire clays are also used. Where non-plastic components are used, the addition of other types of plastic clays – such as ball-clay and non-swelling bentonite can be necessary.

Clay types are very diverse, but can be separated into six different groupings according to their mineralogy (38) (39) (61) (62) as listed in Table 4. The quarried raw materials used in the bodies of building ceramics are usually complex mixtures of clays or argilliferous materials (sedimentary clays, schistous clay, loamy clay, marl quarried from soft and plastic surface deposits to hard mud stones, with other mineral matter such as quartz, feldspars, carbonate minerals, gypsum, metal oxides and sometimes organic matter with shales and marls often quarried from deeper horizons) (63, 64). The American Ries classes clay according to their origin (208) into primary, formed in place by chemical and physical weathering, and secondary clays deposited by erosion or flow of stream away from where it was formed.

Table 4: Grouping of clays showing mineralogical characteristics and industrial applications

Clay Grouping	Characteristics	Utilization
Common clays, shales and marls	Mixtures of differing proportions of clay, including illite, chlorite, kaolinite, and montmorillonite, plus other non-clay (associated) mineral and organic matter.	Cored, hollow and traditional clay products
Fire clay	Found mostly associated with coal measures, Mainly kaolinite in composition and characterized by fine particle-size (providing plasticity), low silica and high alumina composition	Diverse array of refractory products with occasional use for manufacturing masonry products
Kaolin	China Clay: $Al_2O_3.2SiO_2.2H_2O$, white-burning clays formed by weathering of feldspar these rocks, granites, etc. Secondary (sedimentary) kaolins are formed by weathering, then transported and re-deposited elsewhere.	Widely used in the refractory, and sanitary ware industries, plus paper coating, and filler for paint, rubber, and Portland cement.
Ball clay	Common clay minerals ('plastic clays') are hydrated aluminum silicates that have resulted from the weathering of rocks and there are two structural units involved in most clay mineral lattices. One is the 'silica sheet' formed of tetrahedra consisting of a Si^{4+} surrounded by four oxygen ions. The other structural unit is the 'aluminum hydroxide or gibbsite sheet', consisting of octahedra in which an Al^{3+} ion is surrounded by six hydroxyl groups. These octahedral sheets condense with the silica sheets to form the clay minerals. There are a number of mineral species called clay minerals, but the most important, besides kaolin, are 'montmorillonite $Al_2O_3{\cdot}4SiO_2{\cdot}H_2O$ and halloysite' $Al_2O_3{\cdot}2SiO_2{\cdot}3H_2O$	Important constituent of many ceramic bodies - pottery, floor and wall tile, and sanitary ware.
Bentonite	Mainly smectite minerals. A hydrous, clay-like, silicate of alumina, derived from volcanic ash with tri-layered clay mineral montmorillonite ($Al_2O_35SiO_27H_2O$) as main constituent.	Drilling mud, foundry sand, and iron ore pelletizing.
Fuller's earth	$Mg_x.Aly.(SiO_4)_z$ Attapulgite or montmorillonite type clay. Fuller's earth is composed mainly of alumina, silica, iron oxides, lime, magnesia, and water, in extremely variable proportions. It is generally classified as a sedimentary clay.	Used in water and effluent treatment (due to its high cation exchange capacity) and oil and grease absorbents, and pesticide carrier. Serves as a density reducing agent in ceramics.

Research has focused on the shape, design of webs, of products and reduction of material density. The latter has been, since the days of the Poroton patent, mostly been achieved by the addition of organic, combustible, substance of which some are wastes. The research into alternative brick making materials, there is no written law that fired bricks need to be made out of clay, has been, maybe with the exception of the two coal ash brick projects later described (page 43 ff), neglected.

Table 5 illustrates a number of common non-waste additions that have traditionally been mixed to problem clays to improve their brick making performance (65).

In the facing brick and roof tile industry, metallic oxides such as manganese (MnO_2), titanium TiO_2, Fe_2O_3, chromites (iron magnesium chromide oxide $(Fe, Mg)Cr_2O_4$), and minerals such as calcium carbonate ($CaCO_3$), calcium magnesium carbonate ($CaMgCO_3$), can be added to obtain the desired color of the finished product. Barium carbonate (66) (67) might be added to reduce scumming on the surface of the unfired product and later efflorescence of the fired product and to increase production rates by allowing for faster firing.

Table 5: Common non-waste additions widely used in brick manufacture

Material	Characteristics	Utilization
Perlite	A naturally occurring siliceous rock of volcanic origin that, when heated to an appropriate temperature in a counter current free fall kiln, expands up to 20 times its original volume.	Promoting formation of internal pores in the fired product; Fluxing agent; Usually used in its expanded form.
Sand	Sand can be either naturally occurred or obtained as by product from crushing stone. Usually the term sand applies to a granular material in shape not exceeding a grain size of 2 mm.	Provides rigidity to the brick body and increases bulk volume allowing better drying; Increase of density
Ground rock	Ground rock is comparable to sand only that its grain size tends to be coarser than sand.	Provides rigidity to body and increases volume allowing better drying and firing behavior ; Increase of density
Surfactants	Compounds that modify the surface tension of liquids.	Improves forming characteristics, can also enhance drying behavior and reduce shrinkage
Metal oxides		Color enhancement, suppresses surface scumming and efflorescences, improves frost resistance
Carbonate minerals		Color enhancement, suppresses surface scumming and efflorescences, improves frost resistance; Porosity
Organic materials	Straw, sawdust, cellulose, polystyrene	Porosity; Shrinkage

Above is shown, that the introduction of extraneous materials to the clay body used in brick making is not a new idea. However, the approach taken in the research reported herein extends this concept into the use of selected by-products and wastes that are capable of fulfilling these same roles, but extend the possibilities by using such materials as the basis of re-designing the product to achieve production cost reductions, or even additional income, and improved processing properties and particular characteristics, such as low thermal conductivity values, of the finished product.

Organic additions (sawdust, cellulose, formed polystyrene) or inorganic auxiliary agents such as kieselguhr or expanded perlite can be added in order to obtain a lesser body density. In some trials carbonate minerals have been used to decrease density of the clay brick body as the dissociation of oxygen leaves voids in the brick body.

Chapter 2

The case for the use of waste materials in brick

2.1 The case

It is important to distinguish between “additions” to the clay body (such as, for example, saw dust or paper sludge), and “substitutions” (such as, for example, sewage sludge, fly ash or treated aluminum salt slag) that replace a part of the original clay body. The distinction between “addition” and “substitution” for extraneous materials is not always straightforward or easy: An addition might be considered any substance that is added to the original clay body without substitution of clay but modifying its inherent characteristics. A substitution on the other hand may be viewed as any material that for a required volume of brick, reduces the quantity of clay needed to achieve that specific volume target. A substitution can as well modify the clay body.

The guiding rule when choosing wastes and by-products must rest on their compatibility with the original (host) raw material . They must not degrade the final product by focusing simply on making it a repository for wastes (see page 94).

2.2 Wastes commonly used in brick manufacture

The only waste that has gained wide application in the hollow or cored brick industry in general and to a lesser extent in the facing brick industry, is paper sludge both from recycled product[1] and virgin cellulose sources. The use of paper sludge is mentioned, for example, both in the European Best Reference Technique / Best Available Technique BREF/BAT document (48) as well as the Italian BREF/BAT (68).

Product waste generated within the brick manufacturing process itself are also capable of being fully recycled either directly (in case of unfired brick) or or milled-down as grogs and/or chamotte’s.

Other waste from various industries and the service sector, such as ashes from combustion processes, container glass wastes (bottles etc.), ceramic process sludges, water and waste-water treatment sludges, have also been used. Fruit-processing waste, peels and stems, incineration by-products, food processing waste and anaerobic digester residues have all been investigated to some degree and many trialled at the factory scale.

In general, the firing of an aluminum-silicate rich mineral mass such as a brick clay allows the permanent stabilization when fired of almost all included heavy metals except chromium (69)[2]. This statement is true for oxidizing firing conditions as common in most tunnel kilns used for manufacturing cored brick. Moreover, if firing takes place with a reduced percentage of oxygen (reducing conditions) the chromium is usually not oxidized fully to Cr^{VI}. Permanent stabilization is nevertheless not be understood in the sense that the brick can be a repository for wastes.

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[1] A problem with sludge from a paper recycling operation is the use of bleaching agents in the process operation that can lead to damage of the metallic parts in the brick factory dryer and also to detrimentally affect the refractories in the pre-heating zone of the kiln due to Chloride and other bleaching agent residues present in the waste.

[2] On the same subject see also (82), (197) and (198) cited later.

2.3 Addition / substitution of traditional raw materials for hollow and cored brick

Some of the potentially detrimental results on brick products or the production process caused by various wastes can be offset by the use of appropriate “corrective” additives. But such additives have a cost implication that must be offset by the gate fees generated from accepting the wastes to be incorporated into the brick body. If the additional revenue does not cover the expenses for the additives, then from a commercial point of view it is not sensible to consider using the waste.

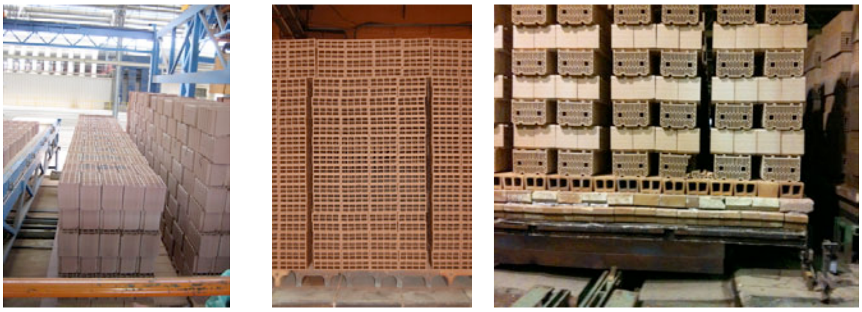
Detrimental effects can include but are not limited to:

- The concentration of chromium and chlorates with respect to their possible volatilization on firing and their subsequent concentration in the flue gases and potential effects on the refractory material of the kiln;
- Odor and smells;
- Heavy metals;
- Organic contamination;
- Chemical contamination;
- Particle-size distribution;
- Water absorption;
- Carbonate minerals content;
- Soluble salts;
- Leaching.

2.4 Energy containing wastes

Reducing the primary energy demand by using energy rich wastes as body fuels is certainly appealing. A side effect of body fuels is always the density reduction of the ceramic body to which they are added. Many of the energy rich wastes in theory promise, frequently substantiated by laboratory testing, considerable fuel savings. More often than not in practice the difficulties and the actual energy savings achieved diminish the appeal and bring an end to the addition of the material. The firing behavior of an energy rich waste added to the clay body in a static laboratory kiln and in an industrial tunnel kiln are completely different: In the counter flow tunnel kiln low temperature carbonization gases emitted from the brick body at temperatures below the ignition point of these gases are conveyed without any effect on the thermal balance of the kiln to the chimney. In the best case these gases are post-combusted in a kiln internal, with a marginally positive effect on the energy balance, or external post-combustion system. In the worst case they are emitted into the atmosphere directly becoming sometimes a heavy burden for the environment and external and internal stakeholders (acrid fumes emitted from the kiln or dryer stack, for example, can be a rather annoying phenomenon). Heat transfer within a tunnel kiln and within the usually densely packed bricks on the kiln car takes place primarily by forced convection of the turbulent kiln gas flow, and, limited to the firing zone, by radiance of the burner flame to the brick. Further heat transfer by conduction from brick to brick occurs at the contact surfaces of the tightly stacked bricks. The latter phenomenon worsens considerably with less dense brick bodies, i.e. brick bodies that contain a substantial combustible content required to reduce density and thermal conductivity.. A number of papers deal with, see Vogt (70) for a rather complete overview of calculation methods, heat transfer within the tunnel kiln. Heat transfer depends also on the way the bricks are stacked, as shown in Figure 2, on the kiln car and the possible surface exposed to convective rather than conductive heat transfer:

Fig. 27: Methods of stacking brick on kiln cars



Vertically stacked brick
VELA S.p.A. San Giovanni plant

Brick stacked in direction of air flow
SBBC Morocco

Brick stacked in direction of flow and at 90° to the flow
VELA S.p.A. Borgonato plant

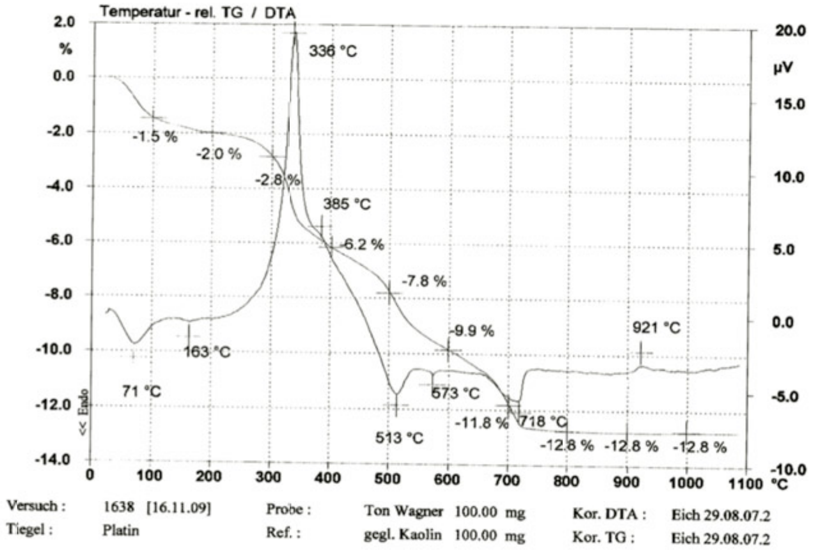
The brick stacked with the cores open in direction of the flow do have a better heat transfer rate than any of the other methods of stacking. The brick stacked in direction of flow and 90° can achieve, if the air speeds in the kiln are sufficiently high to create draft within the 90° turned bricks, acceptable heat transfer rates as well.

The heating up speed of the bricks stacked on the kiln car is not uniform. In the initial phase of the firing process temperatures across the longitudinal and cross section vary, in many kilns, in the range of 100°C to 350°C or even more (see pages 32 and 153 for kiln temperature curves): Processes, for example, release of low temperature carbonization gases and carbonization of organic substances that have already lost their volatile percentage do not occur simultaneously across the same cross section of the kiln car due the temperature differences of the bricks. This is very differently from a lab environment where they occur simultaneously and strictly consequently and well controlled. The non simultaneity makes any process involving body fuels far more difficult to control and govern in an industrial environment than in a lab.

The problems of using of body fuels featuring a high percentage of volatiles is here explained with the example of paper sludge: At a temperature of about 150°C all water that is eventually still present in the cellulose is evaporated. This evaporation process is concurrent to driving out water still present in the clay body and reaches over into the first phases of release of crystalline water. At temperatures between > 100°C and < 375°C volatile substances are being dissociated and evaporate releasing carbon monoxide, hydrogen and hydrocarbons (see DTA's on page 31).

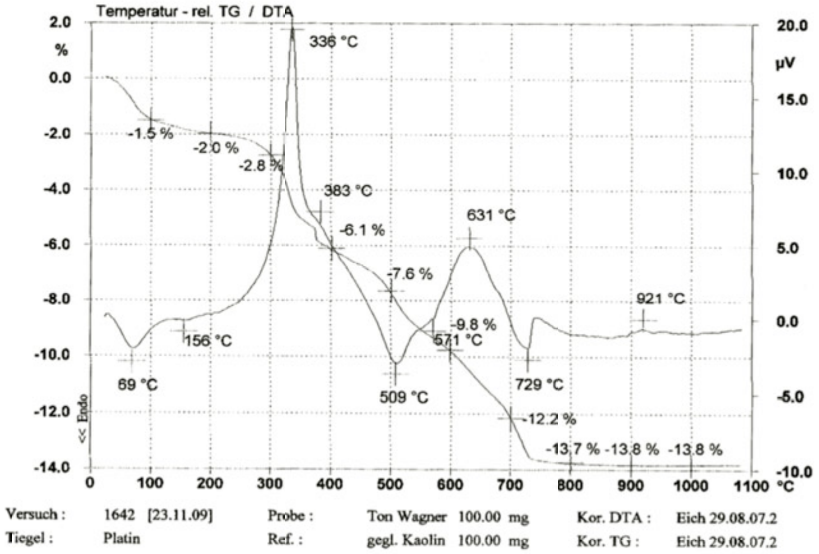
Recently begun research work, not covered in this thesis, by the author shows, the effects of concurrent combustion, a substance with an otherwise higher ignition temperature is ignited by the combustion of the substance with the lower ignition temperature, and impact on the energy balance of a tunnel kiln.

Fig. 28: Brick feed with 20% in volume paper sludge and 1,5% in volume of a bituminous coal



This curve is of particular interest when compared to a curve obtained with the same basic mix but with 1,5% of anthracite, percentage of volatiles < 2,5%, instead of the bituminous high volatile percentage coal of the previous example.

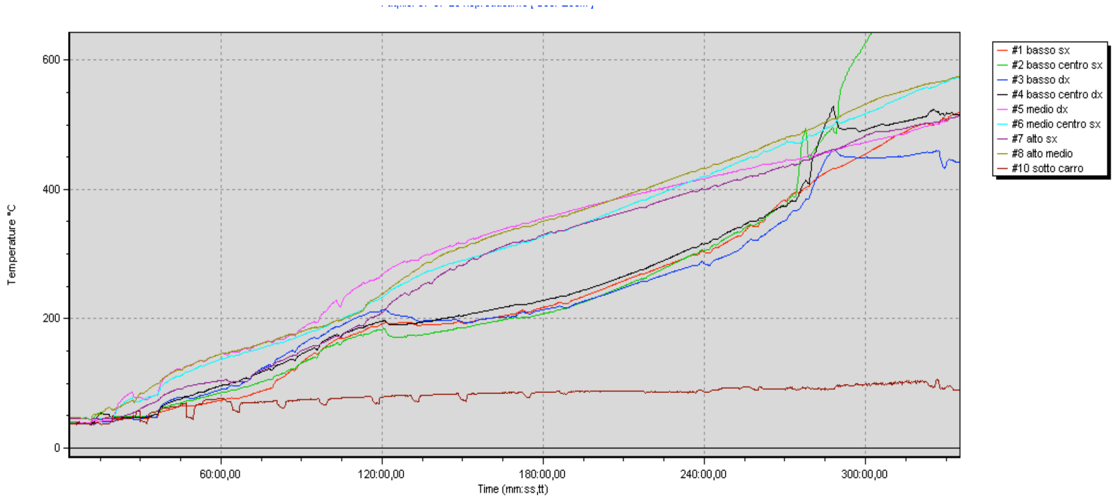
Fig. 29: Brick feed with 20% in volume paper sludge and 1,5% in volume of anthracite



The two curves clearly indicate that a mix of various combustible additions to the brick feed must be carefully chosen. In case two substances both featuring a relatively high percentage of volatile matter but different in their ignition temperature are mixed together as body fuels in a brick, the start of combustion of the substance with the lower ignition temperature will trigger ignition of the substance with the higher ignition temperature. This effect is not observed, when the other substance of higher ignition temperature does feature a very low, like the anthracite in the second diagram above, volatile content. As shown, different ignition temperatures do play a far less important role than volatile content. It is necessary to select carefully mixes of body fuels in order to obtain the maximum effect on the energy balance of the firing process. It appears from these first tests, that the percentage of volatiles plays a predominant role in the energy release of mixes of body fuels.The volatile part of the energy rich additive is usually lost, traditional tunnel kilns are operated in counter flow and hence these low temperature carbonization gases are conveyed towards the stack, and do not contribute significantly to the energy balance of the kiln. The small peak at temperatures between 500°C up to about a maximum of 800°C is caused by the coke like substances trapped in the brick body. The above results indicate that many of the published research about energy rich additions or substitutions to a brick feed are of limited value as not taking into account real industrial conditions.

The firing curve below indicates, for example, that a percentage of the energy containing waste materials mixed to the clay body as body fuel and in substitution of quarried raw materials, especially the upper layers of the brick stacked on the kiln car, has already reacted at temperatures below 400 °C in the preheating zone of the kiln whereas the same material contained in the bricks of the lower level reacts with a sudden release of energy much later in time. At that point the lower and upper bricks on the kiln car reach almost the same temperature.

Fig. 30: Example of a release of energy of combustible organics in a 168 meter Lingl tunnel kiln (VELA S.p.A. Borgonato)



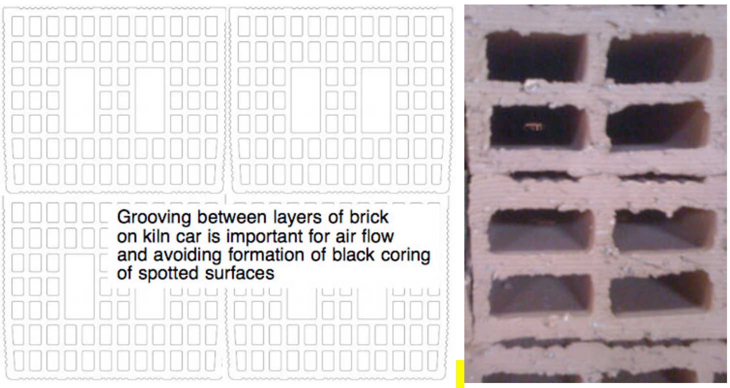
Only at a temperature of about 550°C to 600°C the temperature differences between the lower and the upper layers of the brick stacked on the kiln car diminish considerably. The different line colors each indicate a thermocouple set at a different position in the bricks stacked on the kiln car traveling through the kiln.

These constrains in application of lab results to an industrial process are often overlooked by the various authors making it difficult to scale up research results to a full size production process. Problems with color, cracking and later efflorescence can occur due to interaction. The prospect of having different products (shape, size, thickness of walls and webs, percentage of body fuel) in the kiln at the same time must also be taken into consideration.

A comprehensive investigation in using energy-rich waste additions to clay was carried out by Ziegelwerke Grehl in 1995 (71). However, the results of the study produced little interest within the brick industry at the time as the use of wastes in bricks was considered, and still is, likely to detrimentally affect their "market image"[1]. A very short overview about the study has been published in (72).

Junge in a paper from 2001 states that brick could be fired without the use of external fuels at about 3.3% by mass of coal or 8.3% by mass of sawdust (73). A self firing tunnel kiln would require that enough oxygen for the combustion process is "locally" available. It would hence be required that the stacking of the brick on the kiln car and the outside shape of the bricks allows for sufficient passages to assure sufficient oxygen for combustion (if not pyrolysis is desired that might however leave undesired coal residues in the brick body). This could be obtained by deeper grooving of the shell of the brick, diminishing the area of the surfaces of two bricks in direct contact and thus facilitating air flow around the stacked brick. In the SBBC brickyard, for example, increasing the depth of the groves by about 1.5 mm has been sufficient to reduce or eliminate black coring that occurred due to the combustion of high energy additives, coal and anthracite in this case, on firing.

Fig. 31: Detail of SBBC brick stacked on kiln car with increased depth of shell groves



There is no published research on the effect of the depth of the grooves on the firing behavior of bricks.

2.5 Firing considerations

Brick is fired in a modern tunnel kiln in semi-continuous fashion: the brick is first heated up to the desired firing temperature, kept at this temperature, soaking, for a given and preset period of time, and then cooled down to ambient temperature before it leaves the kiln. A firing curve, increase and decrease in temperature and holding or soaking time that does not fit the material being fired can result in a not be sellable product. For example, large cracks can occur if the temperature increase above 600°C is too fast or if smoking, release of crystalline water occurs once a "closed - i.e. partially sintered" surface of the brick has already occurred . Fine cracks can be observed, for example, if cold air leaks from the stokeholes or from the suspended ceiling in modern tunnel kilns. Different wastes behave differently at different firing temperature – some may disassociate at particular temperatures and liberate volatiles, while others may fuse and become inert and impervious to any later environmental conditions that may be encountered. Hollow or cored bricks are usually fired at temperatures around 825°C to 950°C and although as

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[1] Personal communication by several brick manufacturers (Rimmele, Jungk, Trost) and representatives of the German Brick Association "Grehls research has put in the public the possibilities of using waste. This is not good"

low as 750°C. Production trials with a kiln atmosphere free oxygen content reduced to about 6% have been carried out at temperatures as low as 720°C in the Vela Borgonato plant with a particular low temperature sintering specially designed feed. At these temperatures, provided a sufficient soaking time of about 30% longer than usual is used, brick of appropriate quality could be produced.

The firing temperature ranges for different ceramic products are indicated in Table 6 below.

Table 6: Common firing temperatures of ceramic products in °C

Temperature in °C

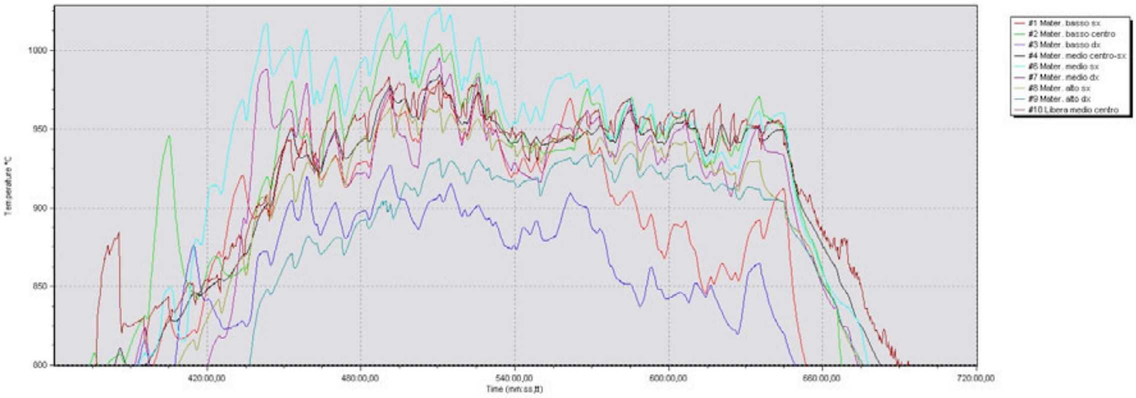
600	650	700	750	800	850	900	950	1000	1050	1100	1150	1200	1250	1300	1350	1400	1450	1500	1550	1600	1650	1700
	Pottery ware							Earthen ware				Vitrous China						High Alumina Brick				
			Hollow bricks, roof tiles, facing bricks (1)																			
							Tiles															
								Klinker														
										Refractories												
600	650	700	750	800	850	900	950	1000	1050	1100	1150	1200	1250	1300	1350	1400	1450	1500	1550	1600	1650	1700

The usual firing temperature for heavy clay products is to be found int he range of 800 to 950°C for hollow bricks. Facing bricks and roof tiles are usually fired at higher temperatures

-1 A firing temperature of 750°C can be achieved with the use of fluxes and particular clay types.

With added body fuels however localized temperatures far higher than the set temperature my be measured due to combustion of the organic matter contained. These much higher firing temperatures will not be indicated by the thermocouples installed on the kiln but can only measured with in process temperature profiling as they are internal to the brick stack.

Fig. 32: Firing zone temperature profile of a kiln set to a 920°C firing temperature in a 168 meter Lingl tunnel kiln (VELA S.p.A. Borgonato)



In the above example the measured product temperatures in the center of the brick stack on the kiln car reached temperatures, especially at the beginning of the soaking cycle, of almost 1,100°C albeit the kiln was set to operate at 920°C. From the same diagram is visible, that the bricks, the blue and green line, stacked in a lower position or close to the plateau of the kiln are certainly, due to a lack of temperature, under fired. The extreme peaks in the lines are due to the thermocouples having been positioned too close to the surface of the brick stack. The sawtooth profile does also indicate, that the burners generate too much specific heat resulting in an over firing of the brick surfaces oriented towards the burner flames. This results in cracking and color defects.

The typical reactions taking place during an oxidizing firing process shown in Table 7 might hence occur even if the set firing temperature of the kiln is lower than the reaction temperature indicated in the table. These divergencies in set and effective and local firing temperature often leads to erroneous interpretation of the origin of firing or cooling defects.

Table 7: Principal reactions of an oxidizing firing process

°C	Effects observed									
100		Residual moisture is driven off			Formation of low temperature carbonization gases			Dissociation of hydroxide and oxyhydrate		
150										Metal sulfate is decomposed starting with $FeSO_4$ at 167°C. $MgSO_4$, $CaSO_4$ and $BaSO_4$ sulfate are usually not decomposed in a standard cored or hollow brick making process due to firing temperatures lower than the decomposition temperatures of these types of sulfate.
200	Beginning of release of chlorates and fluorites					Lime decarbonization	Release of volatile components in the product			
250			FeO content decreases, Fe_2O_3 content increases							
300										
350		$MgCO_3$ is decomposed into MgO and CO_2				Release of crystalline water of magnesia hydroxide that is then available to the matrix as a flux. Might induce formation of a glazed surface				
400				Formation of sulphate with a maximum at 600 °C and 700 °C. Sulfurtrioxides reacts with the still slightly water containing product forming sulfuric acid of varying concentration. This reacts with the calcium carbonate contained in the brick at temperatures exceeding 200°C to					Dehydroxilation – endothermic reaction	
450		Release of crystalline water						Decomposition of pyrite and oxidation		
500										
550					Quartz inversion at 573 °C		Non volatile carbonized components are combusted	Product hygroscopic – absorbs humidity in case firing is interrupted – formation of firing cracks due to slow release of absorbed humidity		
600						Equilibrium phase – material unsusceptible to release of energy from body fuel without any risk to the product.				
650										
700	Combustion of carbon initiates	Release of CO_2 from calcite, dolomite and other carbonate minerals,			Formation of $Al_2O_3Fe_2O_3$ crystals, giving origin of the red color that at higher temperatures decay leading to lighter colors					
750										

°C	Effects observed									
800		$CaCO_3$ decomposes into CaO and CO_2 at temperatures exceeding 825°C		calcium sulphate. At temperatures exceeding 300°C this reaction comes to an end	Dissociation of chloride and fluoride					
850								Formation of Sillimanit from Metacaolin (formed at temperatures of between 550°C and 600°C)		
900	Decomposition of sulfates									
950									Exothermal conversion reactions	
1000			Fe_2O_3 is converted to the dark red Fe_2O_4	Potassium acts as flux if present in sufficient concentration (around 2% min).						
1050										
1100										
1150		Shrinkage								
1000										
950										
900										
850										
800										
750										
700										
650										
600	Quartz inversion at 573 °C									
550										
500										
450		Cooling								
400										
350										
300			Crystobalite conversion (if relatively high firing temperatures over 1,100 °C have been reached							
250										
200										
150										
Out of kiln										

The above table is not specific to a particular clay but rather an overview of the probable reactions at a given temperature. Particular mixes might react substantially differently.

2.6 Status of utility / manufacturing wastes in brick making

The European Directive 2006/12/EC defines wastes as any substance or object in the categories set out in Annex I (of directive 2006/12 EC) which the holder discards or is required to discard. Wastes incorporated into bricks as an addition to the raw materials or as a clay substitute are considered “waste” until fully recovered (in the current instance as component of the fired brick), implying that it no longer poses a potential threat to the environment or to human health. From this point onwards, the waste ceases to be a waste and there is no longer any reason for it to be subject to the controls and other measures required by the Directive. But until the point of recovery, the transport, treatment, management and use of such materials needs to be undertaken in accordance with the relevant regulations and laws.

In most cases waste disposal laws and regulations require that the waste to be disposed of is accompanied by some kind of analytical data. However, such data is generally insufficient to determine whether the waste can be used in brick. For a typical brick factory the information that is required is listed in table 8 below:

Table 8: Basic information for testing the potential waste material for inclusion in a brick body

Oxides & heavy metals	Other	Mineralogy	Impacts
Aluminum oxide Al_2O_3 Sulfur trioxide SO_3 Antimony trioxide Sb_2O_3 Barium oxides BaO Boron trioxide B_2O_3 Calcium Oxide CaO Iron oxide Fe_2O_3 Phosphorus Pentox. P_2O_5 Magnesium oxide MgO Manganous oxide MnO Lead oxide PbO Potassium oxide K_2O Silica SiO_2 Sodium oxide Na_2O Titanium dioxide TiO_2 Zinc oxide ZnO Zirconium oxide ZrO_2 Arsenic As Cadmium Cd Chromium Cr Mercury Hg Nickel Ni Copper Cu Selenium Se Lead Pb Zinc Zn Vanadium V	Humidity H_2O Acidity pH Conductivity uS/cm dry matter % Not combusted % Chloride % sulfur % Fineness (percentage clay minerals if any) Plasticity Firing temperature Mechanical properties at different firing temperatures Calorific value.	Kaolinite % Smectite % Ilite % Muscovite % Chloride % Mica % Fluor %	Odor Odor (on drying) Firing color Shrinkage (extrusion - drying – firing) Cracking (extrusion - drying – firing) Evaluation of possible emissions Evaluation of possible health risks Evaluation of possible financial benefits Evaluation of possible liability risks Leaching of fired product (a standard clay shall be used for this tests in order to assess the leaching addionality of the waste used)

It is essential that the quality and composition of the waste in use at the brick plant must be continuously monitored to be aware of any sporadic fluctuations in composition that could detrimentally affect the manufactured product [(see 74 - included in Appendix V) and (75) and (76)].

2.7 Review of wastes and by-product inclusion into building bricks

This review is not limited to the use of waste inclusion to cored or hollow brick but to brick in general. Pertinent information relating to the published state of the art has been acquired by searching a broad selection of international journals, magazines, books, and advertising material dedicated to this topic and, in addition, the CAS and STN databases. All papers reviewed in this section are grouped according to the source and/or origin and the nature of the waste material they relate to.

In critical examination of this material, it is apparent that the objective of a large majority of the technical investigations have not focused primarily on exploring the potential environmental and financial advantages for the brick maker by adding / supplementing / substituting / replacing traditional brick making raw materials, but rather on assessing their potential in ceramic products as a cheap means of waste disposal or generating income [Scheetz et al. in (77)].

Of all the papers examined few mention the possibility of potentially negative environmental impacts caused by incorporating such wastes. Problems can, for example, arise through:

- Leaching of stored waste materials into the ground or the sewer system;
- Noxious/toxic dryer or kiln emissions into the atmosphere;
- Soil contamination from waste-incorporated products leaching into the soil during their service life;
- Formation of efflorescences on the rendered or original product;
- Worker health issues caused by factory floor exposure;
- Damage to kiln lining refractories or kiln furniture by gaseous substances released from the waste;
- Damage to the dryer furniture by gaseous substances released from the waste;
- Damage to the manufacturing equipment by, for example, impurities.

Most papers also fail to provide adequate information about the possible presence of components that might have “side-effects”. For example, they might promote scumming, which can appear on brick surfaces due to the presence of soluble salts being drawn to the surface during the drying process (118). The possibility of delayed efflorescence is also seldom addressed .

A summary of the most common wastes investigated by various authors are listed in Table 9. This table is mainly compiled from a number of recent general waste utilization overview papers published by Ristic (78), Dondi & Marsigli (79), the Dutch Environmental Protection Agency (80)[1], Junge (81), Andreola et al. (82)[2] and Smith (83). Some waste sources however are not covered in any of the cited overview papers but rather considered in more specific literature. A limited overview of high-calorific wastes investigated in brick making as a body fuel, is given by Köhler (84) indicating also some empirical values for maximum addition of combustibles to the brick body. A very detailed study on

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[1] The only comprehensive paper published by a governmental body on the subject indicating possible environmental effects.

[2] Personal experience suggests that the perspective expressed by Andreola “The ongoing accumulation of industrial waste speaks to the need to seek cost-effective disposal methods. Brick manufacturing would appear to be particularly promising in this regard” is certainly overoptimistic.

various wastes used as body density reducing agents in brick has been published by Krcmar in 2002 (85).

Table 9: Overview of potential waste material considered for inclusion in brick (bibliographic references in brackets)

Source Sector	Material	Referenced in	Additive or supplement	Substitute or replacement
Internally sourced within plant	Clay off cuts	(78) (80) (83)	X	X
Internally sourced within plant (rejected brick)	Fired brick grog	(78) (80) (83)	X	
Construction Tunneling Road works	Spoil soil from excavation			X
Flue gas scrubber waste	Body additive in limited quantities	(83)	X	
Sand / Sand stain Stone cutting sludge	Body additive in limited quantities	(78) (79) (81)	X	
Power or Heat Generation	Pulverized fly ash (PFA) Bottom ash	(79) (80) 82) (83) (85)	X	
Waste Incineration				
Power or Heat Generation	Coke Breeze & Coal Slurry Fines	(79) (81) 82) (85)	X	
Glass	Glass	(78) (79) (80) (81) (83)	X	
Glass fiber Mineral fibers				
Water purification; Industrial and municipal water and waste water treatment	Water treatment residue (WTR); Water cake; Water sludge; Waste water sludge; Waste water cake; Ash	(79) (81) (83)	X	X
Paper manufacturing industry	Paper sludge Paper ash	(79) (80) (83)(85)	X	
Pottery	Glaze Clay Fired ware	(78) (82) (83)	X	
Metal recycling, processing, treatment and metals working	Scoriae Oxides Galvanic sludge Chromium plating sludge Lathe lubricants, way oils etc. Salt slag Foundry sands Foundry slags	(80)(82) (83) (81)	X	X
Food processing Waste biomass	Sugar/Starch oil, alcohol, yeast etc.	(78) (79) (80) (81) (83)(85)	X	
Wood	Dust	(78) (79) (81) (83) (85)	X	
Surface treatment	Powder coatings		X	
Packaging	Polystyrene	(79) (80) (81) (83) (85)	X	
Textile	Dyeing sludge	(81)	X	

Source Sector	Material	Referenced in	Additive or supplement	Substitute or replacement
	Waste fibers and yarns			
Leather (Tanning)	Waste water treatment sludge		X	
Refinery	Whitening earth petrol coke Petroleum waxes	(81)	X	
Drilling	Drilling muds		X	X

A typical example of an instance where there has been a significant amount of academic research into the potential use of a waste material that has never found a widespread application in the brick industry: pulverized fly ash (PFA). The application, is covered extensively in the literature (some references stretch back to the 1950's) and most reports confirm successful use of PFA in the brick industry worldwide. Ashes in general are especially recognized for their good fluxing properties and ability to be used to extend the life of remaining clay reserves.

Incinerated municipal solid waste (MSW) fly ash has also been widely investigated.

In general it can be said that the addition of ash, independent of its origin, leads to a less dense product body with an increased water absorption ratio whilst improving drying behavior of the extruded brick reducing shrinkage with no major environmental or workers safety risks or hazards. Ceramic waste disposal processes for fly ash are not limited to brick: Appropriately standardized ash is used widely in the cement and concrete industry.

A similar situation exists for ground waste glass. In this case although the reasons are more closely associated with economics than on technical grounds. It has been shown in the literature (see 138 to 143) that ground glass is able to achieve positive results as a flux, promoting lower firing temperatures and decreased kiln emissions. The main obstacle stopping the wider adoption of this material in brick making is its high cost much of which is due to the pre-milling operation that is necessary to make it suitable to be added to bricks. Understandably, brick manufacturers are unwilling to commit themselves widely to waste glass as the savings do not currently offer a good financial case. This might change in the future should the cost of primary energy further increase.

A positive example of waste inclusion at the commercial dimension can be found in the use of carbonaceous additives such as coke breeze and coal slurry fines: These materials have been in use for a considerable time in the brick industry. It is likely that they will continue to be used in increasing, especially the low volatile matter quality, quantities, as the cost of premium fuel (gas and oil) continue to rise. Some problems have been encountered with the high concentrations of sulphate that can be associated with these materials that occasionally cause surface discoloration on the ware and increase the level of sulfur dioxide in the kiln exhaust gases. Another positive example is the utilization of many organic wastes generated by the food and beverage industry which possess good calorific values. However, the literature review has highlighted the potential problem of decomposition and the resulting odors associated. Paper waste and paper ash are used increasingly in a similar role too, but problems with heavy metals [from the associated inks (86)] might increase an existing potential leaching problem. Wood in the form of sawdust is also well investigated.

Another question that arises whenever in any of the papers emission into air concentration data are published is: Are these values normalized values, i.e. referenced to a standard oxygen content, or raw measurements (many times without indicating the oxygen content but only the pollutants concentration) and are these values obtained under laboratory or under industrial firing conditions.

2.7.1 Utilization of cut-offs and fired brick grog

The use of clay cut-offs and fired rejected brick as an addition to the brick bodies as shown in Table 10 is state of the art. In some EU countries, for instance Italy, there have been legal problems in the past as authorities held the opinion that the grog would have to be considered (by their interpretation of EU legislation) as hazardous wastes due to leachable chromium and vanadium[1].

Table 10: Utilization of off-cuts and fired brick grog

Source Sector	Material	Potential benefits	Potential Issues
Internal	Clay off cuts	Primary clay / feedstock	none known
	Fired brick grog	Reduction in fired waste	

Fired grog is usually ground and used as chamotte or in substitution of sand, unfired cut offs are usually directly recycled. Dried cut offs or rejected brick are sometimes used to reduce the water content of the feed if this is too high for extrusion.

2.7.2 Utilization of spoil soils

Table 11 summarizes the status of these wastes. For some brick plants the use of spoil soils coming from excavation and tunneling works has become common practice as they have lost, due to the impossibility of opening new quarries, access to own raw material sources but have to rely almost entirely on third party supplies[2]. Sometimes, such as in the case of soil and limes from tunneling works, these raw materials can even generate revenue.

Table 11: Utilization of spoil soils

Source Sector	Material	Potential benefits	Potential Issues
Construction Tunneling Road works	Soil	Substitution of primary clay / feedstock	none known

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[1] In Germany there is currently a discussion that would stop brick waste from being, due to leachable chromium and vanadium content, a recyclable material.

[2] VELA Borogonato and VELA San Giovanni, for example, rely for more than 2/3 of their raw material on various third party sources.

A main prerequisite in brick making is to have a constant material feed. Spoil soils are usually available only in limited quantities and over a limited period of time. The use of such materials hence requires to built up large and carefully planned stockpiles that allow for a sufficient homogenization of the different sources. Sometimes these materials are subjected to waste legislation (for example, spoils from tunneling works if contaminated with other materials). Some very extensive testing of such material has been carried out in connection with the drilling of the AlpTransit tunnel in Switzerland by Rickli et al. (87). The came to the conclusion, that the materials would be suitable for brick making but not for roof tiles.

2.7.3 Utilization of flue gas scrubber waste

Both the VDI 2585 (88) and the Danish EPA - *Kriterier for anvendelse af alternative materialer* (80) indicate recycling of such waste as an additive to the feed as a possible way of disposal (Table 12).

Table 12: Utilization of Flue Gas Scrubber Waste

Source Sector	Material	Potential benefits	Potential Issues
Scrubber waste	Body additive in limited quantities	Reduction of disposal expenses	Scumming, efflorescence, compressive strength, frost resistance

Most brick plants employing such scrubber systems use these wastes even at the risk of generating efflorescences. The mass flow of the waste in relation to the quantitiy of raw materials is usually < 0.5% in mass.

2.7.4 Sand, silt and sludge from mineral processing

The use of fines in either dry or wet form from the stone processing industry is, albeit on a limited scale, common practice in the brick industry and summarized in Table 13 below. These fines are usually inert up to temperatures of about 1,000 °C. Ferreira et al. in (89) state that a relatively high percentage can be used although at the cited firing temperatures of about 1,100 °C thus greatly exceeding today's brick making practice. At lower temperatures the fines usually feature an inert behavior exhibiting a beneficial effect on firing and drying shrinkage and a negative effect on compressive and tensile strength.

Table 13: Summary of sand, silt and sludge from mineral processing

Source Sector	Material	Potential benefits	Potential Issues
Stone processing industry	Body additive in limited quantities	Improves acoustic properties of the finished product.	Characteristics of clay body might change

The use of these relatively dense and heavy materials however might be of major interest when manufacturing bricks or blocks that require superior acoustic properties but of limited interest when thermal insulation blocks are made. The question of carbonates eventually contained in the stonce processing waste must be addressed as well.

2.7.5 Ashes from energy production, waste and sludge incineration

Table 14 summarizes the main uses of ashes, including fly ash, pulverized fuel ash (PFA) and bottom ashes of various origin, in the brick industry.

A detailed report about the use of fly ash in the production of brick has been published by Mörtled and Distler (90)(91). An overview of some papers additional to the ones examined in this chapter can be found in (92) where the production of 100% fly ash bricks is also discussed. A report of laboratory research work followed by industrial trials carried out between 1973 and 1976 is recorded in a 1980 paper (93) by Sajabulatow et al.. Anderson in his 1983 paper (94) indicates the potential risks associated with the use of ashes: The power plant might use coal from different origin fired under varying conditions that might lead to a non constant composition of the ash delivered.

Table 14: Summary of utilization of ashes in brick making

Source Sector	Material	Potential benefits	Potential Issues
Power or Heat Generation	PFA	PFA has a high residual calorific values and can be used up to certain limits as body fuel . Good for multi color products. Sometimes a cheap or even revenue generating alternative to sand used to reduced shrinking and cracking during drying and other drying aids. Fuel content and glass content, body fuel, flux, frit.	Emissions into air; Leaching of heavy metals; Authorizations; Variable composition, low volumes, sporadic supply; Changing calorific value might make kiln control difficult. Changing volatile content might make kiln control difficult. Dust.
Waste Incineration	PFA Bottom ash Ash	Could be used up to certain limits as a body fuel. Good for multi color products. Sometimes a cheap or even revenue generating alternative to sand used to reduced shrinking and cracking during drying and other drying aids.	
Waste water treatment sludge incineration			
Paper manufacturing industry	Paper ash	Body filler and brick body density reducing agent. Small reduction of fuel required to fire body.	
Wood combustion	FA Bottom ash Ash	Body filler and brick body density reducing agent. Pozzolanic behavior	

During the mid 1950’s, when the electricity generating industry in the United Kingdom was still under State ownership, the laboratories of the (then) British Electricity Authority (BEA) began an investigation to develop a commercially acceptable 100% PFA brick. The impetus for this was purely economic (95). It was recognized that such a product would not require clay and could therefore be manufactured at power stations as a new business enterprise. During this development work, 100% PFA bricks (with various bonding agents) were formed by semi-dry pressing. This research was subsequently progressed further by the N.W. Region of the (then) newly created Central Electricity Generating Board (CEGB) (96). After overcoming a number of fabrication difficulties, full-scale making and firing trials were carried out in collaboration with a commercial kiln manufacturer. The physical properties of the experimental bricks produced were proven to be satisfactory. However, difficulties were experienced in bringing the process to full-scale production and particularly the problem of overcoming the obstacle of the very narrow firing tolerance of the bricks which resulted in a high level of rejects (due to both over and under firing) led to the conclusion that the process technology was unlikely to be able to be commercially competitive against normal clay brick products and the project was discontinued in 1961. In the USA, a similar project with the same objective was carried out over the period 1965-72 by the United States Department of the Interior at the Coal Research Bureau of West Virginia University (97). Early realization of the problem of the narrow firing tolerance of 100% PFA bricks ultimately led to the development of a semi-dry pressed product containing approximately 80% PFA and 20% of milled furnace bottom ash (FBA) – a product that was also available abundantly at power stations. This mixture was bonded with ~3% (by dry weight) sodium silicate (water-glass), yielding a brick containing a total of 97% power station ash residue. The inclusion of the coarser FBA helped by creating a more ‘open’ structure which overcame an earlier problem of laminations brought about by air being trapped within the mix during the pressing operation. Moreover, it also had a thermally-stabilizing influence on the bricks during their subsequent firing, thereby avoiding the serious problem of the very narrow firing tolerance encountered in the earlier BEA investigation. The product surpassed all ASTM requirements, such as compressive strength, established for clay bricks in the USA. A pilot plant was then set up to produce this product in sufficiently large numbers to acquire all the technical and economic information pertinent to the proposed establishment of a full-scale factory. Yet, although the experimental product was shown to be substantially lighter than conventional clay bricks and was also comparable in manufacturing cost, the technology was not taken up commercially. One of the main reasons was that in appearance these bricks were very bland compared with existing clay bricks and consequently considered likely to be unpopular if offered on the commercial market. The emphasis placed in the UK and the USA in manufacturing a good quality ash based product has been lost over time. Both the US and the UK project have been geared towards manufacturing a visible to the eye product competing with existing facing bricks. If the research would have been geared towards the manufacturing of hollow brick to be plastered over, the valuation of the outcome of the research might would have been completely different[1].

In 1985 Anderson obtained a patent (98) for a process for making PFA containing bricks to be fired in a clamp kiln.

The other papers examined again mainly see the use of PFA in brick making as way of disposing of a waste cheaply.

Two Japanese papers, both dating from 1993, one by Fujita and Takahashi (99) and one by Fukunaga et al. (100) describe manufacturing of pavers and brick using fly ash. Later papers (101) by Suemitsu et al.., Kusaka [(102) product related] and Kasakura (103) give an overview of the different disposal technologies available in Japan. To emphasize the interest of the Far East region in the disposal of ashes in the brick industry a number of papers are here cited: Kameoka (104) gives a general overview of the potential of re-

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[1] Recently a fly ash based brick manufactured using a mix of hydraulic binders abd bonding agents claiming properties superior or similar to a clay brick has been put on the market by US company Calstar Products http://calstarproducts.com (last accessed January 2010)

cycling of incineration ashes of the incineration and carbonization of livestock wastes. A paper by He et al. (105) states simply that “the bottom (ash) was suitable for beneficial use” although the precise meaning is by no means clear. An overview of recycling different technologies for MSWI ash, among them the use of such ashes in brick making, is given in a paper by Fujiyoshi (106).

Further papers on the subject have been published by Nastro and Gattuso in (107) concerning the manufacture of bricks using three different clays from quarries located in Calabria, a region in the South West of Italy, and fly ash supplied by a nearby ENEL, the national Italian electric energy generation body, power station. A paper published in 1997 by Rincon and Romero (108) in 1997 reported on the use of fly ash in the production of glass ceramics. One by Abrahams et al. (109) deals with the use of incinerator ash for making light-weight porous bricks where a reduction in density was reported to having been achieved, as was also recorded by Barbieri (113). In this case, production of facing bricks, the reduction of density was considered an undesired property. Bozadgiev in his 1989 paper (110) indicates a loss of compressive strength and reduction of density of the clay body when fly ash is used as an additive. Higher levels of inclusion of ashes might result in extrusion difficulties. This can nevertheless be influenced by various additives, for example waste glycerin from the production of biodiesel, if economically viable.

Zrdavkov et al. (111) carried out a number of tests very similar to the ones by (113) with very similar if not the same conclusions: Municipal waste incineration fly ash can be used as a substitute or addition to the clay body of the brick. The percentages used by Zrdavkov are indicated in up to 30% whereas in (113) percentages are limited to 20%. No reason is given in either paper for this limit. The limitations indicate could arise from the extrusion behavior of the brick body determined by the type of clay used in the tests. Papers by Barbieri and Lancellotti (112)(113) deal with the “Incinerator waste as secondary raw material: examples of applications in glasses, glass-ceramics and ceramics” in brick. Another paper co-authored by Barbieri (82) gives a more general overview of the use of wastes in brick. The paper concludes that all the potential waste materials studied (polishing sludge, coal fly ash, steel fly ash and municipal incinerator grate ash) are, with the exception of coal fly ash, suitable for the production of facing bricks. The reason for excluding the coal fly ash is that a more porous brick results. This is certainly an undesired effect for facing bricks but would be greatly appreciated for load or non load bearing cored or hollow brick as it provides a lighter and more thermally insulating product.

A method for manufacturing an aggregate out of MSWI ash is described by Habel (114) without giving any information about potential environmental hazards or or any problems that might be caused through subsequent leaching once in service.

Not only has the use of raw sewage sludge, see section 15 of this chapter, found an academic interest: Sewage sludge incineration ashes have been investigated as well. An overview is given in the conference paper by Suzuki (115) and in the conference report by the University of Hannover – Institut für Siedlungswasserwirtschaft und Abfalltechnik (116). The latter report also includes papers on the use of raw sludge. A paper relating to the risk assessment of using waste water sludge combustion fly ash is that by Miyake et al. (117). These researchers measured radiation from bricks manufactured with and without sewage sludge fly ash and found no noticeable differences. Anderson et al. in (118) also discussed its addition to clay bodies. Environmental issues, such as emissions into air, and product, scumming and efflorescences, are addressed. A full scale industrial test was carried out in an UK brick plant resulting in the production of a large number of bricks. Most interesting is the use, this might have influenced the results of the emissions into air, of carpet yarn as a “stabilizer” for the green brick during these tests. In the Ziegel Gasser Mattoni GmbH S.r.l. brickyard for the same purpose as described by Anderson chopped glass fiber has been used. Most probably carpet yarn does have a beneficial, albeit not investigated, effect on the overall energy consumption of the kiln whereas the glass fiber acts as a frit or fluxing agent. Wiebusch' (119) paper focuses on the reuse of sewage sludge ashes as raw material in the ceramic industry (brick and clay pipe manufacturing). This work is of particular interest as it reports the chemical analysis and particle size distribution of sewage sludge ashes over a one year period. He also investigates the effect of the ash as a fluxing agent. The author states: “The used sewage sludge ashes had higher contents of iron, calcium and phosphorous[1] and a lower silicate content as the used clays”. He specifies, as (109) that ashes reduce the density of the fired clay body. He also investigates the leaching behavior of the brick made with the addition of the incineration ash but does make any assumptions. Wiebusch in an earlier paper written in association with Seyfried (120), investigated “the effects of sewage sludge ashes as additives in brick manufacturing” (manufacturing process itself, properties of bricks and possible effects on the environment). The authors note that the quantity of water required for mixing increases and that lower firing temperatures, due to a fluxing effect of the ashes, result. This fluxing effect has not been investigated by other researchers. They claim that “an increased alkali and earth alkali content of the bricks increases the leaching of trace heavy metals which were immobilized to a large degree by the firing process” and that a “mass balance has indicated that the heavy metals were not released to the waste gas flow”.

A paper by Lin (121) investigates the feasibility of mixing incinerated sludge ash with clay to produce bricks. He investigates the economic aspects of the potential recycling activity as well. Some classification leaching tests on the ash itself have been done in order to characterize the waste. The sludge ash was first combusted at 800° to remove organic matter and then mixed with a ground clay devoid of any analytical data using a crushing machine. The resulting body has not been extruded but cast in hand molds. Each of the molded mixtures was fired in a kiln at temperatures of 950°C, 1,000°C, and 1,050°C for 6 h soaking time. Considering the manufacturing method and the fact that the usual soaking time today is far shorter[2] the results obtained are interesting but of limited value. Plasticity has been investigated stating that both plastic index and dry-shrinkage decrease with an increasing percentage of ash. He found, as the other authors in this section, that the percentage of ash that can be used is in the range of 20% to 40%.

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[1] An increase in the phosphorous content of the feedstock potentially lowers firing temperatures (Seger formula)

[2] Soaking times in modern tunnel kiln in brick making are about 4 to 6 hours for cored or hollow bricks and up to 20 hours or more for facing bricks.

It is unclear wether he refers to mass or to volume. He indicates an optimum firing temperature of 1,000 °C. Interesting is his finding that he had experienced a fluxing effect, without explaining or apparently understanding it, at an ash content of 10 %. This is almost certainly due to accidentally having achieved a chemical composition of the mix that formed an eutectic. Lin eta al in (122) discuss a method for the production of a highly porous pressed, not extruded, paver. The question of producing highly permeable pavers is an important issue in Japan to judge from the papers and patents in this field. Lin & Weng (123) also find positive results, higher compressive strength but this probably mostly due to a reduced water content during manufacturing of the brick, in their research. Environmental aspects are not considered.

The Greater Tokyo Waste Water Management Body had built a pilot scale brick plant to show the feasibility of using incinerated sewage fly ash in brick making. Kraus et al. indicate in (124) that this is common practice in Japan. It has not been possible to find out if this plant is still in operation or if other ways of disposal have been found. No information is available concerning the long term utilization or market of the products manufactured.

Paper ashes are primarily used as a body fuel, filler and pore former for the reduction of the density of the clay body respectively. Their burn-out behavior during the firing process promotes the development of voids and micro-fissures that improve thermal insulation characteristics of the brick.

The use of wood combustion ashes, mainly stemming from community heating plants, can be used as well. The question that needs to be addressed is the slightly pozzolanic behavior of the ashes. This however can be overcome by hydrophobizing the ashes with an appropriate agent such as, for example, a waste glycerine from the biodiesel production. For rice hulks combustion ashes see also (214).

All the papers appear to come to the general conclusion that the use of fly ashes and ashes of various sources is feasible and that, in general, they will have a positive effect on the final product. Such conclusions are confirmed by personal experience.

2.7.6 Carbonaceous wastes

Table 15 records the main features of this type of waste. The use has been first reported in a short journal note dated from 1914 (125). Junge in (73) claims, that an addition of 3,3% in weight of coal would supply all the energy required for firing brick). No bibliographic references are given, but the paper satisfactorily summarizes the (then) state-of-the-art.

Table 15: Summary of utilization of carbonaceous wastes

Source Sector	Material	Potential benefits	Potential Issues
Power or Heat Generation	Coke Breeze & Coal Slurry Fines	Body fuel or fuel, colorant, flux, frit	Emissions into air.

A number of German patents by Poegel (126), Giesen (127), Haessler (128) and Morgante & Haessler (129) dated from 1964 to 1984 deal with the use of coal breeze in brick making. Standing out is the patent by Haessler (128) as it deals not with the addition to the brick body itself but rather filling the voids left in extrusion of hollow or cored bricks with coal before firing the brick itself. Further, a kiln car with a special grooved platform has been developed by Haessler (130) that will allow the use of such materials, either wastes or raw materials, as a fuel[1].

The feasibility of the use of carbonaceous substances as an addition to the clay brick body has been investigated by Andrade et al. in 1994 in (131). The paper cites potentially negative effects in some particularly solid bricks most probably due to thermal conductivity problems within the brick to be fired stacked on the kiln car.

The 1986 paper by Lemaire (132) is reviewed in (79) by Dondi. Ukhin in (133) finds that the use of coal slurries is beneficial for the quality of the brick and Mihailescu (134) et al. arrived at more or less the same conclusions. The production of bricks from coal tailings (washings) is described by Caligaris et al. in the 1990 paper (135) and mentioned by Junge in (81). Their conclusion is that the materials in question can be used for manufacturing bricks without adding clay. No details of any characteristics of the manufactured bricks are given.

Coal breeze has been used in the production of bloated clay granulates for a considerable period, as described by Hedrich (136).

2.7.7 Waste glass

Research has shown that the sodium-lime composition of common glass (containers, plate, automobile etc.) allows for it to act as a fluxing agent and fuse with clay in the production of bricks provided it is sufficiently finely milled. Such an addition can result in a reduction of the firing temperature and hence energy saving benefits. The inclusion of such glass in bricks can also result in increased frost resistance, greater compressive strength, lower water absorption and a decreased tendency to exhibit efflorescence. Waste container glass can have a problem with odor (due to contamination by the remnant product that it contained). Consequently it might need treatment prior to its use in the brick manufacturing process. Table 16 records the main features, benefits and issues surrounding its use:

Table 16: Summary of utilization of waste glass

Source Sector	Material	Potential benefits	Potential Issues
Recycling of glass	Glass	Fluxing agent, reduced emissions, reduced fuel and increased product technical specifications. Some potential for drying. Needs to be a fine powder.	Varying composition of waste glass might cause difficulties in use. Dust.
Recycling of glass fiber	Glass	Fluxing additive, reduced emissions, reduced fuel and increased product technical specifications. Some potential for drying. Needs to be cut to appropriate length.	Dust.

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[1] A kiln to this principle has been in operation in the Hilti, Mettauer GmbH, plant in Götzis in Austria. The kiln has, as stated in th press by the managers of the plant, that the kiln has never delivered the expected and agreed performance driving the company into receivership. (http://www.ksv.at/KSV/1870/de/5presse/2medienarchiv/1insolvenzerstfaelle/2010-09/ZIEGELEI/index.html)

Brinkler comments in his 2004 paper (137), that the high cost of milling the collected waste glass to a sufficient fineness has hampered its more extensive use. He assumes that the use of waste glass as an addition to the brick body would reduce manufacturing costs, due to lower firing temperatures, by about 1 to 1.5% using a 5% addition of waste glass. Financial information are also given in a paper by Gupta and Arozarena (138). They indicate the potential saving of energy to be about 10 to 15% using 15% of waste glass and claim reduced, also by 15%, firing times and hence greater production. Given the difference between the two results presented, such results need to be verified before considering the use of waste glass in a brick plant. This could only be done on an individual factory by factory basis, as clay type, product type, kiln design etc. will all be influencing factors. Tests by the author do no substantiate either claim to the extent mentioned.

Comprehensive tests to demonstrate the commercial viability of incorporating ground glass into bricks have been carried out at CERAM Research under the direction of Smith (139) (140). The results showed the beneficial effect of the use this material. Smith also reported (141) about the use of particular glass wastes, such as cathode ray tubes (CRT), which he deems, contrary to (81), as potentially beneficial for use albeit waste legislation problems would have to be overcome. A project concerning the use of CRT and container glass as a sole raw material for bricks, pavers and slips as been carried out by Anderson et al. at Staffordshire University (142) that resulted in the establishment of a purpose company for the manufacture of such products[1].

The use of waste glass when used as a fluxing agent, frit[2] or as a substitute for sand, should be considered ‘state of the art. A number of patents: Hatomi (143), Sokolov et al. (144), Read and Anderson (145), Chen (146), Xu (147), Johns Manville Europe (148), Akita et al. (149) and Kato (150), mostly focusing on a particular source of glass in various forms and shapes and eventually some additives used in preparing the body such as in (145) by Read and Anderson, have been granted a patent and one is pending. The content of the patent (148) by Johns Manville Europe is in many ways similar to the later one submitted by Smith (151) summarizing previous well known state of the art claiming intellectual rights for it[3].

Glass can improve the characteristics of otherwise unsuitable clays as, for example, described by El-Mahllaway in (152). Papers which indicate the positive effect of ground glass on the sintered clay body have been published by Yourkevich et al. (153), Fukunaga et al. (154) and Leshina (155). An interesting approach is reported by Pontikes at al in (156) using a soda-lime glass derived from urban waste, hence not a waste glass in the narrow sense, as a frit. He observed effects that one would expect when using a classical frit in addition to a clay body.

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[1] Geofusion Ltd.http://www.geo-fusion.co.uk (last accessed January 2010)

[2] Depending on the chemical composition of the body.

[3] “*The invention relates to a method for manufacturing a brick, ceramic or similar article. Traditionally the manufacture of bricks, roobacfing tiles and pipes has been an energy intensive process. Increasing commercial and environmental demands are drivers to reduce energy requirements the generation of so-called greenhouse gases. By the addition of finely milled glass, as a fluxing agent, the firing temperature has been reduced. This has had the added benefit of reducing fluoride emissions from the articles during firing. The invention overcomes problems associated with the prior art by providing a method for manufacturing a brick or similar article comprising the steps of: producing a clay mix by mixing milled clay with a fluxing agent, forming the mix and firing it to produce finished brick or ceramic articles, characterized in that the clay mix is capable of being fired at a lower temperature*” The cited paper by Gupta and Arozarena (138) might invalidate any claim made by Smith in his patent.

The following results have been obtained in laboratory tests:

Table 17: Glass addition to brick feed fired at three different temperatures

Firing temperat-ure	Sample	% H_2O	% shrinkage dry	% shrinkage fired	Density in kg/l	Compressive strength in N/mm^2
910°C	Reference mix	19.90	4.70	4.80	1.640	100.10
	Reference mix + 2% glass	19.60	4.80	4.80	1.659	103.35
840 °C	Reference mix	19.70	5.30	5.10	1.667	99.29
	Reference mix + 2% glass	19.20	5.30	5.40	1.000	108.67
780 °C	Reference mix	19.70	5.30	5.10	1.684	57.59
	Reference mix + 2% glass	19.20	5.30	5.00	1.687	81.87

The addition of finely ground recycled glass increased mechanical resistance at lower firing temperatures. The findings confirm the literature data.

The use of waste glass fibers as an additive to the brick body has apparently not been investigated. The influencing behavior of ground glass and glass fiber might broadly to be considered to be the same. The major difference is, that glass fiber normally has a substantially better consistency with regard to its chemical composition than recycled and ground glass from varying sources.

Table 18: Glass fiber addition to brick feed fired at 920°C

Sample	% H_2O	% shrinkage dry	% shrinkage fired	Density in kg/l	Compressive strength in N/mm^2
Standard feed	16.76	4.67	4.64	1.882	9.242
5 % in volume fiber	17.25	4.11	4.10	1.866	8.969
10 % in volume fiber	17.16	3.89	3.88	1.850	8.434
15 % in volume fiber	17.91	3.78	3.70	1.826	8.084
20 % in volume fiber	17.87	3.66	3.74	1.750	7.467
10 % in volume fiber + 5 % in volume paper sludge	18.06	4.14	4.15	1.811	7.930
10 % in volume fiber + 10 % in volume paper sludge	18.76	4.37	4.22	1.756	7.582
15 % in volume fiber + 5 % in volume paper sludge	18.96	4.36	4.25	1.750	5.803
15 % in volume fiber + 10 % in volume paper sludge	19.18	4.28	4.35	1.636	3.600
15 % in volume fiber + 10 % in volume saw dust	19.25	4.70	4.53	1.756	7.604
15 % in volume fiber + 10 % in volume saw dust + liquid silicate	18.53	2.87	2.97	1.703	5.006
15 % in volume fiber + 20 % in volume saw dust + liquid silicate	19.63	3.28	3.40	1.594	4.463

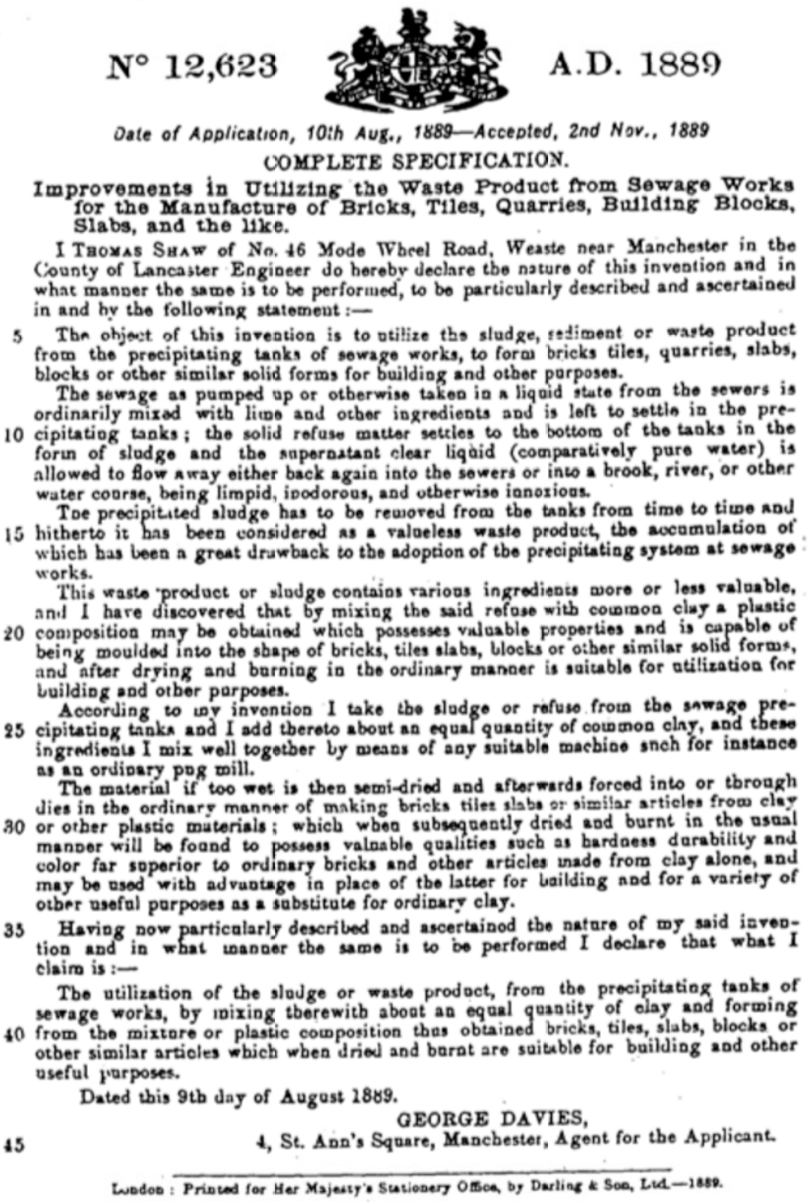
In these tests, a sensible reduction in density is always associated with a sensible reduction in compressive strength. The results reported above show clearly, that down to a certain density glass fiber alone is a far better density reducing agent that a combination of fibers and any of the more common density reducers. As the glass fiber itself is not releasing any energy during the firing process and furthermore acts as a frit, it must be said that its addition especially to low density mixes might be very welcome.

Despite the positive effects, the use of glasses has not found a wider application.

2.7.8 Drinking water and waste water treatment residues

The very first patent for the use of raw waste water treatment sewage sludge as part of the body of a brick went to Shaw (157) in 1899.

Fig. 33: Facsimile of the original Shaw patent



N° 12,623 A.D. 1889

Date of Application, 10th Aug., 1889—Accepted, 2nd Nov., 1889

COMPLETE SPECIFICATION.

Improvements in Utilizing the Waste Product from Sewage Works for the Manufacture of Bricks, Tiles, Quarries, Building Blocks, Slabs, and the like.

I THOMAS SHAW of No. 46 Mode Wheel Road, Weaste near Manchester in the County of Lancaster Engineer do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement :—

The object of this invention is to utilize the sludge, sediment or waste product from the precipitating tanks of sewage works, to form bricks tiles, quarries, slabs, blocks or other similar solid forms for building and other purposes.

The sewage as pumped up or otherwise taken in a liquid state from the sewers is ordinarily mixed with lime and other ingredients and is left to settle in the precipitating tanks; the solid refuse matter settles to the bottom of the tanks in the form of sludge and the supernatant clear liquid (comparatively pure water) is allowed to flow away either back again into the sewers or into a brook, river, or other water course, being limpid, inodorous, and otherwise innoxious.

The precipitated sludge has to be removed from the tanks from time to time and hitherto it has been considered as a valueless waste product, the accumulation of which has been a great drawback to the adoption of the precipitating system at sewage works.

This waste product or sludge contains various ingredients more or less valuable, and I have discovered that by mixing the said refuse with common clay a plastic composition may be obtained which possesses valuable properties and is capable of being moulded into the shape of bricks, tiles slabs, blocks or other similar solid forms, and after drying and burning in the ordinary manner is suitable for utilization for building and other purposes.

According to my invention I take the sludge or refuse from the sewage precipitating tanks and I add thereto about an equal quantity of common clay, and these ingredients I mix well together by means of any suitable machine such for instance as an ordinary pug mill.

The material if too wet is then semi-dried and afterwards forced into or through dies in the ordinary manner of making bricks tiles slabs or similar articles from clay or other plastic materials; which when subsequently dried and burnt in the usual manner will be found to possess valuable qualities such as hardness durability and color far superior to ordinary bricks and other articles made from clay alone, and may be used with advantage in place of the latter for building and for a variety of other useful purposes as a substitute for ordinary clay.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed I declare that what I claim is :—

The utilization of the sludge or waste product, from the precipitating tanks of sewage works, by mixing therewith about an equal quantity of clay and forming from the mixture or plastic composition thus obtained bricks, tiles, slabs, blocks or other similar articles which when dried and burnt are suitable for building and other useful purposes.

Dated this 9th day of August 1889.

GEORGE DAVIES,
4, St. Ann's Square, Manchester, Agent for the Applicant.

London : Printed for Her Majesty's Stationery Office, by Darling & Son, Ltd.—1889.

In 1975 a patent for sludge incorporating brick was granted to Lingl in Germany (158) and in 1978 (159) in the USA. There is no record of bricks being subsequently made commercially following either patent.

The main characteristics, potential benefits and potential issues of theses wastes are summarized in Table 19. Potable water sludge or waste water treatment sludge usually possess a high content of clay/silt. The centrifuged or filter-pressed sludge typically contains > 75 % water. The use of sewage sludge could certainly have a beneficial application in bricks as a result of its calorific value, even if a large percentage of the organic content is highly volatile, and advantages on extrusion and drying behavior of the brick due to fats and proteins contained in the sludge. This provided a solution to the odor problem can be found and the reluctance of the workforce in handling it, can be overcome.

Table 19: Summary of utilization of water and waste water treatment residues

Source Sector	Material	Potential benefits	Potential Issues
Water purification;	Water cake; Water sludge;	Fluxing colorant, revenue, formation of micro pores in ceramic body leading to better insulation values of the fired product. Reduction of fuel required to Fired body.	Carbonate minerals might be source of efflorescence
Industrial and municipal water and waste Water treatment	Waste water sludge; Waste water cake		Industrial and municipal waste water sludge or cake might contain certain heavy metals, especially chromium that can lead to efflorescence of the fired product. Certain substances used in the treatment such as carbonate minerals might have a detrimental effect on the fired or green body. Some issues with emissions into air.

When using waste water treatment sludges the first question to be answered is, if the sludges are anaerobically digested or raw: Digested sludges usually feature less problems due to a reduced bacteriological activity. The odor for digested sludges is generally not considered noxious but only unpleasant whereas non digested sludges usually are a source of a substantial odor problem and require a costly and intensive odor treatment[1]. A practical use of sewage sludge as a clay substitute is made by the Algoa brick plant in South Africa using non pre-treated sludge (160), by Ziegel Gasser Mattoni GmbH S.r.l. employing an odor treatment process patented by Moedinger and Gasser (161)(162) and by Recuperi Industriali S.r.l. in preparing a clay substitute mix for VELA S.p.A. brick plants. Algoa claims a substantial reduction in the primary energy need of the brick firing process by > 65% (On the issue of bricks containing sufficient body-fuel of this type to reach the point of being "self firing" see (163) by the Lingl company and (84) (85) and (269) for the maximum energy content in an unfired brick body in a traditional tunnel kiln) whereas for Ziegel Gasser Mattoni GmbH S.r.l. the reduction of quarried clay and density is of far greater importance. The treatment procedure adopted also ensured that the hygiene requirements and health and safely issues are satisfactorily addressed (164). Brosnan (165) in 1992 used in his tests a sewage sludge from the experimental VerTech deep well oxidation of sewage sludge process. Churchill in his 1994 paper (166) gives a good, even enthusiastic, overview of the challenges and benefits of using sewage sludge as an additive to a clay body. No analysis of the used sludge is given. A 1986 patent by Hashimoto et al. (167) lists a considerable number of trials and their results (albeit

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[1] In most of the papers reviewed in this section the origin of the waste water treatment residues, digested or non digested sludge, is not quite clear. Almost never it is indicated if and which thickening or precipitation agents mostly have been used in the sludge conditioning process. No paper has been found that deals with the effect of the different precipitation agents on the brick production process. Should the use of sewage sludge as a clay substitute advance, certainly further research is needed.

the firing temperatures are all well over 1,000 °C). This patent is geared mainly to the use of sewage sludge in the production of pavers. A paper dealing with the question of using sludge in brick making in general, was published by Gobold et al. (168) but nevertheless fails to address the problems of the development of carbonate minerals that arise during firing, which could cause scumming and efflorescence on the dried green or fired bricks. Additional papers have been published by Prouty et al. (169) and by Aleman (170)(171). In these latter papers deal the author define the use of sewage sludge as a "containment", suggesting the prime objective of their paper is disposal. However, he does give particular attention to the exothermal effects occurring during firing (presumably in a batch kiln). Also Almeida et. al (172) are in search for a cheap disposal instead of considering sludge a raw material. The conclusion that waste water sludge can successfully be used in brick making is shared by Yokota et al. (173), Shin et al. (174), Balgaranova et al. (175), Anderson et al. (118) and Geuzens (176).

The chromium leaching problem, non soluble forms of chromium are oxidized to the soluble chromium^{VI} on firing, is a concern when using waste water sludges. A careful selection of the sources is necessary. The chromium leaching problem is explained in a paper by Van der Zwan et al. (177). These researchers suggest that the firing of the brick product has to take place under reducing conditions to avoid a soluble form of this metal being created. A simplified approach, similar to the one in (232), is taken by Belyakov et al. in (178). A non published paper indicates a color change risk (179). With possible emissions under oxidizing firing conditions when using sewage sludge deals a paper by Cusido et al. (180). The conclusion is clearly that a number of pollutants are found when firing the sewage / clay mix that are not found when firing the clay alone. These differences found however are to be deemed laboratory values. Under normal production conditions at Ziegel Gasser Mattoni GmbH S.r.l. first and VELA S.p.A. later, such differences have not been found. The firing tests would have been of great interest if any information about brick/air ratios and λ-values of the burners would have been published. As they are, they are only a rough quantitative comparison of eventual emissions in batch firing.

The only paper concerning the use of sewage sludge that reaches an overall negative result is the one by Mesaros (181) in which he reports on an actual production trial in which a substantial loss of quality of the bricks was recorded.

A potentially interesting alternative for the use of sewage sludge in a brick plant has been done by Rieger (182) in 1985. He demonstrated that sewage sludge could be successfully pyrolysed and the resulting gas used to fire a brick kiln while the resulting wastes could be added to the feed.

Hasegawa et al. in their 1977 (183) paper investigate the use of sludge cake deriving from water potabilization.

From the treatment of fresh water used as cooling water in thermal power stations a very fine silt sludge is obtained. This can be beneficially used as a clay substitute in brick making. The problem is the usually relatively high water content of this sludges of around 30 to 40% in weight. These sludges are used by the author since 2007.

A thesis paper by Kraus (184) focuses on the so called PORODUR pyrolysis process of manufacturing an aggregate out of sewage sludge and waste glass. The product would not have been brick but rather a ceramic low density aggregate similar to bloated clay.

2.7.9 Paper sludge

The use of paper sludges as additives to brick and/or tile bodies is very well established in a number of European countries. In Table 20 the main characteristics, potential benefits and possible drawbacks are summarized. In Germany (and Austria, Switzerland and France as well) a considerable percentage of the paper sludge available on the market is now used in brick making[1]. In contrast, in Italy, although the 1992 paper by Tenaglia et al. (185), substantial industrial interest has not appeared until relatively recently. One problem is that while paper sludge is normally produced all year round the brick factories, at least in Northern Europe, are not operating over the full year. This might have helped to induce the paper industry to search for alternative ways of disposal. In addition there are difficulties due to the chemical and microbiological decomposition of the sludge that usually leads to a disagreeable odor. Another aspect relating to the successful utilization of this waste in brick manufacture concerns the problem of the de-inking and bleaching agents used. These chemicals when becoming volatile in the dryer at higher temperatures or at the beginning of the firing process can be the cause of serious corrosion in the kiln and drier.

Table 20: Summary of utilization of paper sludge and ash

Source Sector	Material	Potential benefits	Potential Issues
Paper manufacturing industry.	Paper sludge	Low grade body filler and brick body density reducing agent. Reduction of fuel required to fired body.	Paper sludge from waste paper might have an issue with bleaching agents that might lead to corrosion in the kiln, kiln equipment or dryer. Some issues with emissions into air.

The fibrous nature of the paper sludge reduces shrinkage and cracking during the drying operation. The various approaches used in applying this technology at factory scale and the nature and characteristics of the products, are contained in a number of published papers which also record the ‘state of the art’ between 1991 and present. Ducman and Kopar (186) examined both the use of sawdust as well as paper sludge in the production of low bod density clay bricks. Szucs and Badacsonyi (187) considered the environmental aspects of its use in the building industry, while Zani et al. (188) (189) looked at the full-scale factory aspects of using paper sludge from recycled paper with Geller and Bienert (190) giving a general overview about the use of paper sludge in Germany. Liaw et al. (191) describe a method for manufacturing low density ceramic aggregate similar to bloated clay from paper sludge and co-generation ashes. Similar methods (192), mixing ashes with paper sludge, are cited by Kraus (193). The 1991 Greengrove (192) patent precedes the paper by Liaw (191) but is not referenced by the latter. Information on

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[1] For example, in 2000 in Germany 24% of all paper production wastes have been sent to brick plant. 26% of all wastes have been used as fuel in plant owned combustion plants. The remaining volumes have been sent to landfill, cement industry and composting. Landfilling, accounting for about 15% of the total volume, has been terminated in 2005.
Statistical data published by the Landesamt für Natur, Umwelt und Verbraucherschutz Nordrhein-Westfalen

changes in the compressive strength due to the use of such products can be found in Krcmar (85).

2.7.10 Pottery waste

In most areas where brick making is carried out there is not a large enough pottery or white wares industry to contribute significant tonnages of waste. Table 21 overviews the main types, potential benefits and possible restrictions.

Table 21: Summary of utilization of pottery waste

Source Sector	Material	Potential benefits	Potential Issues
Pottery waste	Glaze Clay Fired ware	Fluxing body additive Plasticity, green strength Drying properties	The quantities of pottery waste available are usually to low to be used to any major benefit.

The only problem that might be encountered in its use is one that could arise through the incorporation of ground glazed ware which due to a high level of heavy metal (especially chromium) may cause leaching problems in fired bricks containing them. However, overall, in comparison to the total throughput of raw materials at a typical brick plant, the potential advantage of using these wastes is negligible.

2.7.11 Metal processing and metal treatment wastes

The main characteristics, benefits and potential issues of using wastes produced by this industrial sector are summarized in Table 22. The attractive colors of porcelain products manufactured by the white wares sector of the ceramics industry are manufactured using a wide variety of metal oxides. The same oxides can also be used to modify the color of bricks. However, due to their high cost, the only feasible way of acquiring them for this purpose is in the form of waste streams arising from an original production operation.

Table 22: Summary of utilization of metal processing and treatment waste

Source Sector	Material	Potential benefits	Potential Issues
Metal processing	Oxides	Colorant	Undesired heavy metal concentrations.
Metal treatment	Oxides Galvanic sludge Chromium plating sludge	Colorant	Undesired heavy metal concentrations.
Aluminum recycling	Salt slag	Density reduction	Smell

None of the papers examined, except one by J. M. Magalhaes (194) deals with the leaching behavior of different oxides. The different sintering behavior arising from the different proportion of clay matter and oxide-containing metal treatment sludge(s) is also well explained in the paper.

The use of general waste generated in the metal working industry is described by Stanaitis et al. (195) in their paper. In the tests discussed, the researchers added metalworking wastes in excess of 1.5% (in weight?) to clay bodies. This addition resulted in widely varying compressive strength values. The tolerances might be due to poor mixing of the samples. In industrial production mixes prepared under the direction of the author at Recuperi Industriali S.r.l. and employed in Vela S.p.A. brick yards, such differences have not been found[1].

A patent (196) by Hanaoka and Saiki describes the coloring effect of metal containing waste (oxides) on clay bodies. Another one by Ramos da Costa and Ferreira (197) focuses on the use of brick as a 'repository for heavy metals' but fails to address the environmental impact of such a procedure especially as far as chromium is concerned. In another paper Ferreira et al. in (198) describe results of tests carried out incorporating galvanic sludge without any reference to the possible future leaching behavior of the hexavalent chromium from the brick product.

The use of copper ore waste products was briefly investigated by Bozadgiev and Dimova in (199) without any indications about the results.

The potential utilization for the production of an "ecological brick" using a low-zinc carbon dust generated in electric arc furnaces is described by Domínguez and Ullmann (200). As to be expected, barium, cadmium, lead and zinc are permanently bound in the ceramic process. Chromium is mentioned as well but does not seem to pose a problem as the values measured are far below the adopted and pertinent regulatory levels.

Aluminum oxide, mixed to SiO_2 and metals, from the secondary aluminum reclamation industry is obtained after the processing of waste saline slag. This material is very refractory, but can potentially be considered as a filler or grog in brick products. However, it has a odor issue due to the release of ammonia fumes. These ammonia emissions can present a substantial health problem if not treated. Some tests with aluminum salt slag resulted in the following:

Table 23: Aluminum salt slag addition to brick feed

Sample	% H_2O	% shrinkage dry	% shrinkage fired at 920°C	Density in kg/l	Compressive strength in N/mm^2
Standard feed	18.69	5.39	5.26	1.797	9.114
Standard feed with 5% volume aluminum slag treated with 0.2% acetic acid	18.94	4.66	4.53	1.716	8.568
Standard feed with 5% volume aluminum slag treated with 0.2% phosphoric acid	18.89	4.62	4.74	1.701	8.113
Standard feed with 5% volume aluminum slag treated with 0.2% borate	18.72	4.71	4.35	1.682	7.829
Standard feed with 5% volume aluminum slag treated with 0.2% acetic acid + 0.2 % borate	16.61	4.55	4.25	1.681	8.931
Standard feed with 19% volume aluminum slag	19.67	3.75	3.84	1.590	6.334

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[1] Quality control VELA S.p.A.

Sample	% H_2O	% shrinkage dry	% shrinkage fired at 920°C	Density in kg/l	Compressive strength in N/mm^2
treated with 0.2% phosphoric acid + 0,2% & borate 5%					

A patent for a method for the ammonia release treatment of aluminum salt slag has been applied for. There is also a problem of soluble sulphate present in this material that may cause kiln scumming and subsequent efflorescence once in service.

In general it appears from the literature that the possible use of waste metal oxides in the enhancement of the color of brick products is an established technology. However, concerns about the future recyclability, with particularly focus on wastes produced by the galvanic and similar industries which frequently contain high concentrations of chromium, remains a contentious issue and a serious concern.

In using such materials there is however a major risk of obtaining bricks with substantial efflorescences or color problems:

Fig. 34: House built with bricks containing metal working wastes (chrome plating)(Northern Italy)

Greenish veiling, due to chromium leaching, is clearly visible on the non rendered brick surface. These veiling could in the end become, after some time, visible on the rendered surface as the chromium salts slowly migrate to the surface.

The idea of using waste foundry sands to replace otherwise specifically quarried sand, could have considerable environmental benefits if the potential hazard of increased radiation levels and unknown organic and inorganic components would not subsist. None of the authors address these problems. In Table 24 the major effects and benefits are listed.

Table 24: Summary of utilization of foundry waste

Source Sector	Material	Potential benefits	Potential Issues
Foundry	Sand	Substitution of raw materials	Wear and tear on equipment.

In the paper by Pezarski et al. (201) from Poland the percentage of foundry sand that can be used is given as 20 %. A paper dealing with the general feasibility of using foundry sands in brick making, even the ones apparently containing furan resins, has been written by Milani and Milani (202)[1]. Certain zircon sands, a component of some

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[1] Foundry sands do exhibit, experience gained at VELA, due to mixing of various additives such as synthetic resins, for example, a very unpredictable behavior in firing due to an unknown release of energy. This can lead to formation of coring and de-

sands used in foundries, do exhibit a natural radioactivity. One researcher (203) has measured radiation from zirconium in tiles and found values that are in the range of roughly $^{1}/_{10}$ of the radiation released during a classic X-ray. Quality controls of the fired and ready to sell brick[1] show that in certain cases an important level of radiation can be measured [see (204) and (205) for some reference on natural radiation of brick].

The use of foundry sands at the Vela S.p.A. Group San Giovanni del Dosso plant led to significant surface de-coloration problems:

Fig. 35: Color effects on brick surface due to the use of foundry sands

As it appears from further testing that foundry sands can have a positive effect as well. The problem is that these need to be managed very carefully. The sands have to be free of fines and the radioactivity level checked. The varying energy content, granularity and composition of the sands is also a source of further problems.

2.7.12 Food and drink processing waste

A problem frequently encountered with food processing wastes is their biodegradation. This process usually commences within a short period. Some of these effects, such as for example the generation of alcohol from fruit wastes, can have a positive effect (on extrusion and drying behavior). No adverse emissions to the environment would be expected from the use of such wastes. However, odor can be considered a potential problem with organic wastes. Table 25 summarizes the main types of this class of organic wastes that are commonly available. Sugar and starch wastes are the most attractive brick making additives arising from the food processing industry. Other wastes, such as filter residues containing sugar from the production of fruit concentrates are also of value if available. This latter by-product is used by the Ziegel Gasser Mattoni GmbH S.r.l. brick plant as an additive to the brick body and is discussed more fully in a later chapter of this thesis. It consists of expanded perlite, which acts as a low quality flux, Fuller's Earth, which serves as a density reducing agent, plus sugar and organic fibers which give marginal contribute to the strength of the unfired bricks.

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coloration. Albeit it is suspected that in many cases foundries use the sands as a mean for disposal of other wastes such as oils. Due to this uncertainties the use of foundry sands is, once existing contracts have been terminated, is discontinued at VELA. It has further been found that foundry sands, most probably due to the raw materials used for the foundry parts, cause the fired brick to feature radiation levels exceeding the allowable limits.

[1] Quality control VELA S.p.a.

Table 25: Summary of utilization of food and drink processing waste

Source Sector	Material	Potential benefits	Potential Issues
Food processing wastes	Sugar/Starch oil, alcohol, yeast, oils, fats	Anti scumming additives, green strength, extrusion aid, body fuel	Odor

Another possible waste source are the by-products arising from the olive oil industry. This is a mixed material of two distinct phases produced during the olive milling process. While the solid phase has a high calorific value and can be used as body fuel, the liquid phase (sometimes called blackwater) can replace all the normal water used in the brick extrusion process, as described by Mekki and Anderson et al. (206) and Trifilio (207). In the role described by Mekki and Anderson it assists extrusion by its lubricating properties. Commonly, the liquid waste has a low pH value of 2.5 to 3,0. Low pH values can have a beneficial effect on drying (208)[1]. Analysis on the same product carried out in Morocco by SBBC (209) show a potential contamination with arsenic. However, nowhere else in the examined literature has further evidence been recorded concerning this problem, although phenols are recognized to be present. Blackwater production tests carried out in 2008 at the Vela Borgonato plant gave the following comparative results:

Table 26: Comparative data standard brick / blackwater added brick

Sample	% H_2O	% shrinkage dry	% shrinkage fired at 920°C	Density in kg/l	Compressive strength in kg/mm^2
Standard feed	17.60	4.70	+ 0.1	1770	106.02
Standard feed added 3.5% in volume blackwater	19.45	5.60	0	1726	104.82

The product characteristics did not change sensibly. The energy absorption on the press did however diminished considerable by about 50 Amps on average[2].

Waste beer yeast has been used in the Baustoffwerke Hüning GmbH brick plant (210) for some time until the associated odor problem became too severe. Utilization of brewery wastes more in general, including paper bottle labels, have been investigated by Knirsch et al. (211). The results, considering that the waste contain a large percentage of kieselguhr, the results in density reduction, see also (85) on density reduction with kieselguhr, are well within the range of what can be expected. The assumption of the bricks loosing color upon firing due to the addition of the paper from the labels and some types of glue associated with it, is certainly wrong. It could be that potassium drying efflorescence, visible only after firing, has been observed but not recognized as such.

Junge in (81) gives some reference to the use of wastes from the edible oil industry. The results reported by this paper indicate that the waxes contained in the waste have a stabilizing effect during the brick drying operation and that they reduce shrinkage (a similar effect is observed if waste glycerin from the production of biodiesel is mixed to the feed). They also increase porosity upon firing, hence reducing the product thermal conductivity.

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[1] The modification of pH values of bodies has not been investigated since the publication of the cited publication of Singer and Singer albeit the potential it posses appears important.

[2] Tests carried out under the supervision of Prof. M. Anderson and Prof. G. Skerratt of Staffordshire University.

The effect on drying can be explained due to the waxes not shrinking during the drying process, hence forming a stable framework within the bricks. The effect of the waxes on porosity is due to their combustion during the firing operation.

The use of risk husks, in practice in certain brick yards in Italy (212), has been subject of research in the main rice growing countries like India. Dondi (79) makes reference to one of the two papers of Rahman (213) and, for rice hulk combustion ashes, (214). In the first paper reference is made to a paper (215) by Pepplinkhouse in which the latter describes in detail an industrial test. As an aside here, it would have been helpful if Pepplinkhouse had also measured and reported shrinkage. The utilization of rice husks is also reported by Sabrah et al. (216) in Egypt.

Coconut waste as an addition to the clay body has been investigated by Warrier et al. (217) and does demonstrate a behavior in line with other ligneous brick body density reducing agents. The same authors have published another paper (218) in 1988 on the same subject. The use of palm kernel shell as fuel for burning bricks has been investigated by Obeng et al. from Ghana, This is certainly a noteworthy example for a third world country trial of making brick making more sustainable both from an economic as well from an environmental point of view (219). In India nut shells are used as fuel. In Morocco the utilization of peach pits is under development as a substitute fuel within a Clean Development Mechanism (CDM) project (220) (221) (222).

2.7.13 Wood waste (saw dust)

Wood dust (or sawdust) is a common and widely used combustible and density reducing addition in brick production (Table 27). It might be defined only in certain conditions as waste as in many cases saw dust is outright purchased and delivered to specs.

Table 27: Summary of utilization of wood waste

Source Sector	Material	Potential benefits	Potential Issues
Wood	Dust	Body fuel, green strength, brick body density reducing. Better drying behavior.	Some issues with chemical contamination (glues, paint, etc.). that might have an impact on emissions into air.

In brick making untreated hardwood saw dust is best used. Saw dust from coniferous wood can contain essential oils in relatively high concentrations that might have an impact on the emissions into air of the plant. Saw dust from recycled wood should be avoided as there is always the risk of material contaminated by oils, paint, solvents, glues etc. that might result in undesired surface effects and emissions into air.

A useful comparison between different body fuels including sawdust is reported in a paper by K. Mueller et al. (223)[1]. A patent by Krause (224) is also recorded for the use of tree bark as a body fuel. Murray and Liversidge (225) go as far as to investigate the shape of saw dust with reference to its usability. Albeit of great scientific interest, the paper is certainly too theoretic to be applied in the day to day operation of a brickyard. Practical research results can be found in a paper published by Isenhour (226).

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[1] Mueller claims, that untreated, crushed lignite was the best body-fuel available.This is certainly not surprising considering the low percentage of volatile matter of lignite in general.

2.7.14 Surface treatment and packaging waste

Polystyrene packing waste might well be described as the most common waste, besides paper sludge, used in brick manufacturing.

In Table 28 a general overview is given.

Table 28: Summary of utilization of surface treatment and packaging waste

Source Sector	Material	Potential benefits	Potential Issues
Surface treatment	Powder coatings	Body fuel, green strength, brick body density reducing agent	Some issues with heavy metal content. Emissions into air.
Packaging	Polystyrene	Body fuel, brick body density reducing agent	Some issues with compressive non proportional reduction in compressive strength Emissions into air.

Including the Poroton[1] polystyrene process, patented by the Swedish engineer Sven Fernhof in 1958 (227), in this literature review might appear at first sight a bit far fetched. Poroton is the first patented density reduction process in brick making and has gained wide acceptance. In most cases today the expanded polystyrene used is sourced from waste streams and hence the inclusion of the Poroton process has been deemed appropriate. A very good overview of the technical effects of the addition of polystyrene to bricks is given by Veiseh and Yousefi in (228) without making any direct reference to the original patent. Krcmar in (85) has investigated the effects of various brick body density reducing agent agents on the mechanical properties of brick. He found substantial differences in compressive strength of the brick when using recycled and freshly foamed polystyrene.

Given their calorific potential powder coating waste could be very interesting but their classification as “dangerous” (EC waste code 080112) makes them unattractive.

A number of tests with powder coatings have been carried out at Ziegel Gasser Mattoni GmbH S.r.l., Baustoffwerke Hüning GmbH and JUWÖ Poroton Werke Ernst Jungk und Sohn GmbH. The problem that emerged was, that the chemical composition and heavy metals content varied considerably with the color of the powder coatings waste. A patent by Park (229) describes the use of this waste as a “catalyst” but does not offer any explanation about the catalytic reaction. The effect of using such material as an odor inhibiting agent has been undertaken at the Baustoffwerke Hüning GmbH brick plant in Germany in 1991 (230) by mixing the waste powder coatings with sewage sludge. The inhibiting effect might be most probably due to the pH value of the powder of 10 to 11 in an aqueous solution hence creating an alkaline environment.

Preliminary tests with powder coatings added to a standard brick feed at Ziegel Gasser Mattoni GmbH S.r.l. resulted in some very interesting results that, due to legislation in Italy classifying such wastes as hazardous, did not find any practical application. Powder coatings are thermosetting at temperatures in the range of 80°C to 200°C. Calorific values and combustion behavior are similar to finely ground coal. The tests have been car-

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[1] Poroton is registered trademark

ried out with a carboxyl group terminated polyester resin with primid, a hydroxamylkylamid, as bonding agent[1]. The density is to be found between 1.4 and 1.5 kg/l. In Table 29 a general overview is given.

Table 29: Analysis of powder coatings

Impact category	Unit	Concentration measured
pH in water		7,5 – 9
Incombustibles at 99°C	%	99,20
Incombustibles at 600°C		27,90
Benzene	mg/kg	3,9
Toluene		48,00
Ethylbenzene		12,00
Xylene		19,00
Styrene		< 10,00
Ethanol and ethanol compounds		< 10,00
Propanol and propanol compounds		< 10,00
Butanol and butanol compounds		< 10,00
Acetate and acetonic compounds		< 10,00
Phenol and phenolic compounds		< 0,1
Σ Cadmium		< 1,00
Σ Chromium		< 50,00
Lead		< 650,00
Copper		< 130,00
Arsenic		< 100,00

Emission tests have been carried out with an addition of 10 to 12% in volume. The tests have been carried out at temperature of 391 °C, the peak energy release temperature, see the DTA's Fig. 28: and Fig. 29: on page 31, for substances with a high concentration of volatile compounds. The tests suggest, when compared to the standard emission values of Ziegel Gasser Mattoni GmbH S.r.l., kiln equipped with an internal post combustion system, that an use of these substances would have been feasible and certainly, from a financial and technical point of view, interesting. The average grain size dimension of the powder coatings is by far inferior to the average grain size of saw dust and hence a far higher compressive strength values for a same density would have had to be expected (but these have not been tested for). Brick densities achieved have been more or less similar to the densities achieved with the use of saw dust. No chemical analysis has been made on the finished brick.

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[1] Manufacturers data

Table 30: Flue gas concentrations at 391°C

Impact category	Unit	Raw gas concentration measured	Raw gas concentration standardized to 18% O	Gasser values (after post combustion)
Oxygen	%	19.4		
Carbon monoxide	mg/Nm³	67,00	42.43	8
Σ C		34,00	21.53	Not measurable
HCl		3,50	2.21	< 50
Vinyl chloride	µg/Nm³	< 30,0	19.00	No data
Formaldehyde	mg/Nm³	< 2	1.26	< 0.01
Acrolein		< 1	0.63	No data
Plasticizers of various types	µg/Nm³	< 100	< 63.33	No data
Benzene		616	390.13	< 100
Toluene		221	139.96	No data
Ethylbenzene		52	32.93	No data
Xylole		174	110.20	No data
Styrene		54	34.20	No data
Naphthalene		54	34.20	No data
n-Alkane		332	210.26	No data
Methlyacetate		< 10	< 6.33	No data
Ethlyacetate		112	70.93	No data
Butylacetate		< 10	< 6.33	No data
2-Butanone		169	107.03	No data
Olefines / Paraffin e(C1-C5)	mg/Nm³	< 0,05	< 0.03	< 1
Methane		< 10	< 6.33	No data
Ethane / Ethene		< 10	< 6.33	No data

The analytical flue gas concentration data certainly suggest that with an appropriate post combustion system, such as the one installed at Ziegel Gasser Mattoni GmbH S.r.l., the use of such additives would be possible without any harm to the environment as the values would certainly result much lower than the allowed emissions.

2.7.15 Textile wastes

The limited consideration in general literature of leather tanning sludge are due to the usually very high chromium and sodium concentrations. These will lead to undesired leaching (177). In some countries there is also a problem with sodium arsenite, sulphides and other chemicals used when tanning leather.

Table 31: Summary of utilization of textile sludge

Source Sector	Material	Potential benefits	Potential Issues
Textile	Dyeing sludge Fibers	Body fuel, brick body density reducing agent	Odor. Potentially heavy metal content from dyes. Certain waste could have an effect on emissions into air.
Leather (Tanning)	Waste water treatment sludge	Body fuel, brick body density reducing agent	Odor. Potentially heavy metal content from dyes. Certain waste could have an effect on emissions into air. Corrosion of kiln equipment.

A paper by Basegio et al. (231) refers to the problem of chromium solubility under standard oxidizing (non reducing) firing conditions. In addition emissions were also tested. It was found that zinc and chlorine were not immobilized but released during firing. It was therefore considered that the release of chlorine might, under certain conditions, lead to the formation of dioxins and furans[1]. Under normal conditions such releases might also be a cause of corrosion within the kiln or the kiln / dryer system. A paper from Hellinger (232), sponsored by the original waste producers research institute, the Forschungsinstitut für Leder- und Kunstledertechnologie GmbH (research institute for leather and leatherette) and hence with the clear goal to propose cheap ways to get rid of a big problem, goes as far as to envisage some kind of “job sharing” between a tannery and a brick plant.

Textile sludges, for example, from the stripping of wool, is a lesser problem compared to tannery wastes. A paper by Kumar et al. from India (233) explains that bricks have been manufactured using textile sludge and that no negative effects on the physical characteristics of the brick have been found. Another paper detailing the potential of wool scouring effluent is the one written by Ferrero and Marchese (234). This paper is the basic idea behind the trials at RIL – Rondi Industria Laterizi where such sludges have been used for some time (235) until its use has been suspended by local authorities due to odor problems. This appears to be a reoccurring problem with all such organic sludge when stored and used in the brick making process. Subsequent environmental issues, such as leaching or a negative contribution to kiln emissions, are not discussed in the paper and were also not investigated during the RIL- Rondi factory trials.

The use of carpet yarn is described by Anderson in (118).

2.7.16 Refining wastes

Refining wastes are not only available from the classical refining of crude oil but also from the production of biofuels.

Due to the high content of combustible substances in the Fullers Earth used in refining operations, the possibility of future interest from brick manufacturers as a means of dis-

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[1] This problem might also arise in the use of paper sludge in a similar fashion.

posal seems, provided the waste can be classified as a non dangerous waste, possible. Table 32 summarizes the state of the art.

Table 32: Summary of utilization of refinery waste

Source Sector	Material	Potential benefits	Potential Issues
Refining of fuels and similar	Whitening earth	Body fuel, brick body density reducing agent, substitution of raw materials	Odor. Potentially heavy metal content from dyes. Certain waste could have an effect on emissions into air. Corrosion of kiln equipment. Color
	Petroleum coke	Body fuel, substitute for fuel	CO_2 and SO_X emissions. A potential problem with the refractories due to vanadium swelling.
	Petroleum wax	Body fuel brick body density reducing agent agent Plasticizer Mixing water control	Potentially heavy metal content from dyes. Certain waste could have an effect on emissions into air. Corrosion of kiln equipment. Color
	Glycerine	Body fuel, brick body density reducing agent, drying	PH-value, Chloride

Some research, although not directly relating to bricks, but containing indications of the properties of whitening earth have been published by Sun, Sun et al. (236) (237) (238) and by Monteiro et al. (239).

Another refinery by product is petroleum coke, or petrol coke. In Spain, as Brosnan reports in a paper published in 2007 (240), the use of petrol coke as a body fuel implies frequently some visible disadvantages such as a change in color. Such changes have however not been observed by the author in other brick plants in Italy and Morocco making use of petrol coke as body fuel. The changes in color Brosnan observes might be due to inappropriate firing conditions of the brick. The use of petrol coke as fuel is, at least in certain countries, relatively common. Some petrol cokes can contain up to 7.5% of sulfur and almost 6% of ash (241) and hence can eventually cause damage to the kiln refractories due to swelling of vanadium contained in the refractories. A problem with the use of petrol coke is also that the firing capacity per burner in a tunnel kiln is limited to about 65 kWh of energy. A modern high speed gas burner delivers up to about 250 kWh. The use of petrol coke burners is hence limited to the soaking zone of a tunnel kiln. A further issue is, that the pressure within the kiln will need to be augmented causing, in some kilns, the risk of a damage to the suspended ceiling as this is not designed to withstand such pressures[1].

A single paper deals with the use of straight chain high-melting petroleum or slack waxes that still do contain a substantial percentage of oil and are as an additive to brick feeds that apparently have a positive effect on changing plasticity and reducing density. In the

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[1] In 2008 a large section of the ceiling of the number 2 EquipCeramic brick kiln installed at SBBC in Morocco had to be substituted due to damage caused by excessive pressure in the kiln resulting from the use of petrol coke burners. These burners need relatively large volume of air and a very strong circulation within the kiln the function properly and guarantee uniform firing of the product.

paper by Almeida (242), indicating the composition of the used clay as well and firing the samples at a common temperature of 920°C, some examples of density reduction are given. Thermal conductivity of the brick samples has been measured as well and compares favorably.

Brosnan[1] in 2007 investigated the possible use of glycerine as fuel for the brick industry. Tests by the author in the Ziegel Gasser Mattoni GmbH S.r.l. brick plant in 2006 resulted in extensive white spots on the bricks exposed to the flame due to glazing with the salt contained in the glycerine. Eventual corrosion to the kiln itself or to ducting or burners due to the salt content could not be verified during the 10 days test. The direct use as fuel appears, based on this experience, to be be of limited interest if no appropriate and special technologies are developed. A problem, at least in Europe, might be the patent submitted by RWE (243)[2].

The rapidly growing production of biodiesel from oil seeds and rendering fats has created a relatively large offer of glycerin. Testing of an addition to the clay body has taken place at the Vela S.p.A. Corte Franca plant. This type of glycerin, either further refined to increase the pure glycerin content, or in its original form, occurs in a 10:1 relationship. The non refined waste glycerin is characterized by the following analysis:

- Glycerin 82 to 85 % in mass;
- Methanol < 0.1 %;
- Organic, non glycerol substances, MONG < 1.5%;
- Salts < 7%;
- Water, difference to 100 %;
- ph value 7 to 8.

This analysis applies to the glycerin used in the tests derived from production of biodiesel from rapeseeds. Should biodiesel of any other origin be used, the analysis can differ substantially. Comparative tests with glycerin from a different source have not been carried out. This glycerin has been used as an addition to the brick body itself. In the Vela Borgonato plant a raw material mix with a fired density of 1.625 kg/l is used. This mix contained about 18% in non quarried secondary raw materials.Two trials with different dosages of waste glycerine have been carried out: The first test was run using 0.02% by weight referred to the wet feed, in the second 0.05% was used. Both tests have been run over 2.5 three shift days and resulted in:

- Lesser power requirement of the extruder at the almost same cutting frequency but at higher extrusion pressure;
- Reduction of the water content of the brick by 2.5 % to 3.0 % in weight;
- Reduction of drying cracks;
- Reduction of phosphate efflorescences on the surface of the brick;
- Substantial modifications to the firing curve with a substantial release, indicated by a peak in the firing curve, around 350°C to 450°C.

The use of such substances appears to be of interest. However, no industrial application has yet been identified.

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[1] Not published paper

[2] The patent has been , 2011,withdrawn

2.7.17 Drilling muds (oil & gas drilling)

A limited interest in using such wastes in brick making does exist. Some testing has been done within the industry. Table 33 records the main features, benefits and issues surrounding the use of this by-product.

Table 33: Summary of utilization of drilling muds

Source Sector	Material	Potential benefits	Potential Issues
Drilling	Mud	Substitution of raw materials Body fuel brick body density reducing agent	Emissions into air

However, the potential of their utilization in the brick industry has been investigated in some papers mostly from Brazil, for example, the one by Jorado and de Oliveira (244) where the problem of disposal of these wastes appears to be more stringent. No information about the effective use of such sludges in brick making in this country or other areas of the world is available.

A paper by Steiner from former Yugoslavia (245) deals with the addition of used drilling fluids to brick. No real conclusion about any potential use is drawn.

The paper by Souza (246) indicates that the maximum addition to a feed should not exceed 5% in weight in order to avoid detrimental effects on the brick. A paper published later by Monteiro (247), very critical of the aforementioned paper, comes to an entirely different result using apparently similar clays and similar technologies.

None of the above papers explore the potentially hazardous effects of emissions into air or the issue of worker safety.

The oil based muds (248) are frequently made up of long chain hydrocarbons (C12 – C16) and hence they exhibit a combustion behavior that can be compared to other oil based extrusion additives used in the brick making process. The water based muds, apparently not having presented a disposal problem, have not been investigated until recently.

2.8 Other waste materials / mixes of wastes

Sludge from harbor or river excavation has been repeatedly used in trial productions of bricks. In (249) and in (250) Bäätjer and Detzner claim its beneficial use in brick making. The firing temperature required is in the region of 1,100 °C and the soaking time typically 72 hours. A research project by the University of Bremen[1] investigates the use of harbor sludge as well. Their findings are summarized in several papers (251) (252) (253). The German construction company Züblin filed a patent for the production of a bloated aggregate based on excavated sediments (254) in 1983. The same year Mijnster filed a patent (255) in The Netherlands claiming technology and process also indicated in the Züblin patent. Cool and Rang (256) registered a patent for the use of dredging and harbor mud mixed to industrial and/or water treatment sludges and/or fly ash also from in-

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[1] Institut für Geo - Chemie

cinerator plants for the manufacturing under oxidizing firing conditions, no reference to chromium leaching is made, of principally non-building ceramic products such as pipes, road construction (in whatever shape?) and dikes.

Some tests with a mix of different refinery wastes and sewage sludge have been made by Balgaranova et al. (257) indicating the potential for density reduction of cored bricks with mixes made of up to 10 % sewage sludge and 10 % refinery wastes.

The CEGB filed a patent (258) for a fuel ash added clinker material in 1979 that was granted in 1981 for a mix of fly-ash and sewage sludge albeit the intended product is not shaped ceramic bodies but rather an aggregate for concrete.

Mixing of a dry matter such as fly ash to a wet substance such as sludges of any origin and adding a fluxing agent to improve firing characteristics is a very basic technology and apparently has, in various forms, been the subject of some research targeted at obtaining positive financial results. None of the patents cited has lead to any commercial application.

The use of mineral fibers, rockwool namely, as and addition to a brick body has been described by Bachmann et al. in (259). This allowed a further reduction in the quantity of thermal energy required by the manufacturing process. The German company Wool.rec GmbH holds a patent (260) for a pore former made of recycled mineral wool bound with clay and water glass.

Last in this list of examination of wastes and/or by-products are the instances where the brick is considered to be a safe repository for dangerous substances. In this context the term “dangerous” is not used in a purely technical or legal manner: A substance that from a purely technical point of view might be considered eligible to be incorporated into a brick might not be so from the producers perspective. Such a controversial product would be asbestos for example. Tamas et al. in their paper (261) claim that asbestos can be used safely in a percentage as high as 10 % (presumably in weight but not specified) as an additive to a clay body if temperature, they indicate 1,000 °C, and soaking time at this temperature, which they do not indicate, is high respectively long enough. At a temperature of 900°C they indicate a loss of ignition of the brick of around 20% (for two samples even at 1,000°C). Italian originated patents, (262) and (263), by Plescia et al. claims the production of filtration elements by mixing ground asbestos waste with clay and then firing the mix at 1,000 – 1,200 °C. Complete inertness is claimed. In 1993, Born and other coworkers have obtained a patent for the incorporation of asbestos waste into bricks after treating the asbestos with fluorine containing acids (264).

2.9 Conclusions

From this survey of international literature, integrated with some unpublished material test data obtained by the author it can be seen that a substantial range of by-product wastes can be used, or are being considered for use, in brick manufacture.

In summary, a number of broad conclusions can be drawn:

- Careful investigation, testing and mix design is required before using mixes of various waste additions or substitutions in order to obtain the optimum energy yield and product quality;
- Some wastes, such as clay off-cuts and crushed brick (grog) are an intrinsic part of the everyday by-products arising from the brick manufacturing process. As in the past, they will continue to be recycled back to the beginning of the process-line;
- Sand is a common ingredient in brick making and has always been a relatively cheap material to import into the factory. However, today there is increasing environmental concern about the quarrying of many sand deposits. The replacement of this virgin material by either, observing the necessary precautions, recycled foundry sands or, better because of the lesser risks associated, ashes, is shown in literature;
- The availability of very large tonnages of fly and other combustion ashes from various sources and their widespread geographical location internationally, offers considerable scope as a long-term accessible by- product. Their ceramic characteristics are covered extensively in the literature. Ceramic waste disposal processes of fly ash are not limited to brick: standardized (265) fly ash is used widely in the cement and concrete industry. Other processes, such as the only laboratory scale VitroArc processes described by Haugsten and Gustavson (266), are also available for the treatment and safe disposal. In general it can be said that in the papers reviewed so far, the general results are that the addition of ash, independent of the origin of the ash, leads to less dense product body but higher water absorption ratios whilst improving drying behavior and reducing shrinkage and with no major environmental or workers safety risks or hazards. The many reports examined, confirm their successful use in the brick industry worldwide. These by-products are especially recognized for their good fluxing characteristics and ability to be used in conjunction with clay to extend the life of remaining clay reserves;
- Waste glass has been shown to be able to achieve positive results as a flux, promoting lower-temperature firing and decreased kiln emissions. The main obstacle stopping its wider adoption in brick making is its cost, much of which is due to the high level of pre-milling that is required to make it a suitable fineness to be added to bricks. Also contributing to the high price is the competitive demand by other industries that are able to pay more for it. Understandably, brick manufacturers are unwilling to commit themselves widely to waste glass as the savings do not currently make a good financial case;
- Carbonaceous additives, such as coke breeze and coal fines, have been in use for a considerable time in the brick industry. It is likely that they will continue to be used in increasing quantities, as the cost of premium fuel (gas and oil) might again rise in the future. Some problems have been encountered with the high concentration of sulphate sometimes associated with this material which can produce surface discoloration on the ware and also increase the level of sulfur dioxide in the kiln exhaust gases;
- This is also the case for many organic wastes produced by the food and beverage industries which have substantial calorific values albeit their use is due to the high volatile percentage usually not contributing substantially to the overall energy balance of the firing process but can cause emission problems. However, the literature review has highlighted the potential problem of decomposition and the resulting odors associate with these by-products. Paper waste and paper ash are used increasingly in a similar role too, but problems with heavy metals (from the associated inks) have been recorded as producing

potential leaching problems. Wood in the form of sawdust is also well investigated, but non-continuity of supply and variability in quality have caused problems with efflorescence;

- Paper waste and paper ash, are reported to be being used increasingly in a similar role, but problems with heavy metals (from the associated inks) have been recorded as producing potential leaching problems;
- Wood in the form of sawdust is also well investigated, but non-continuity of supply and variability in quality has caused problems with efflorescence;
- The question of chromium and vanadium leaching must be addressed. From miscellaneous references in the surveyed literature, it would seem that the leachability of hexavalent chromium is strongly influenced by the mass relationship of $CaO:SiO_2$ and the alkali metal oxide concentration. Hinz and Press in their patent address the question of "encapsulation" of heavy metals (267). Again the main focus is on disposal but not on substitution of raw materials. Stube in (268) applies the same idea of encapsulation, most heavy metals are permanently bound within the ceramic matrix, principles as those expressed in (197) but claims that by following the patented procedure there would be no risk from leaching.

The literature has also revealed a large number of 'minor' wastes with a potential use in brick making such as pottery wastes, metal processing residues and textile sludge. In many instances there are limited quantities of a specific waste available and this will therefore restricts their use to those brick plant in reasonable proximity to the waste generating industry.

What is certain is that, increasingly, new sources of potential usable wastes will be under investigation by the brick industry. This will be initiated both as source of additional revenue (via a gate fee) or because they can improve certain characteristics of the existing products. The waste inclusion work undertaken by the candidate at the Ziegel Gasser Mattoni GmbH S.r.l. brick plant is original as confirmed by the afore literature survey. It is consequently likely to be replicated more and more frequently, as the serious issues of energy conservation and raw materials sustainability, become even more crucial to the brick industry. This presents a demanding challenge in the attempt by the industry to survive amid a growing number of alternative building material now available on the market, which in many cases are cheaper and possess improved specifications.

The unanswerable question is why this technology is not of greater interest to the brick sector as a whole. Usually, "universal" solutions such as the case of the use of paper sludge, are constantly being searched for. Individual solutions are not of interest. The answer may lie in the limited technical and analytical capacities of the single, smaller plants. But then, the large industry groups do not show any major interest either, so this cannot be the whole story.

Chapter 3

A South Tyrolean Case Study: Mattoni Gasser Ziegel GmbH S.r.l.

Advances in the utilization of waste materials and energy sources in brick making

Impacts

3.1 Ziegel Gasser Mattoni GmbH S.r.l.

In 1889 a mason named Josef Gasser, not related to today's brick yard's owners of the same name, built the first seasonal brick kilns in the area. Shortly thereafter he substituted them with a coal fired Hoffmann kiln. In 1915 his company was taken over by the “Vereinigte Pustertaler Ziegelwerke AG S.p.A.”. After their bankruptcy in 1932, the plant in Schabs / Sciaves was bought by the today's owners family. The Gasser's of these times used to be inn keepers and farmers who had rented out land to the bankrupt company.

Fig. 36: The Vereinigte Pustertaler Ziegelwerke brick plant around 1925. In the foreground the naturally vented dryer and in the back the building hosting the Hoffmann kiln

In the early years the company employed well over 100 workers and was for many families the only source of income in an otherwise rather barren area at that time.

In 1964, one of the first of the type in Italy, an Ing. Jäger Nürnberg built tunnel kiln substituted the Hoffmann.

Fig. 37: Aerial views of the brickyard (left picture: on the left the brick yard and to the right the village of Schabs / Sciaves)

3.2 Business evolution assessment

Bricks are a low added-value product with very limited profit margins that leave little or no space for maneuver. Even minor glitches can result in a financial loss. Terms of payment are, at least in Italy, usually 90 or even 120 days invoiced at end of month thus requiring the brick plants to either to have access to substantial credit lines or dispose of sizable amounts of cash.

The Ziegel Gasser Mattoni GmbH S.r.l. brick company focuses on brick as its principal source of turnover. The principal sources of profit are however waste recycling and the sale of aggregates. In addition the company partners in a ready mix concrete company to which it supplies aggregates.

Starting in 1999, forced by the market situation deteriorating because of the ever growing influx of brick from both Germany and Austria, the Ziegel Gasser Mattoni GmbH S.r.l. r owners were forced to review their trading position. The company, historically in a position of manufacturing monopoly in the region, had decided not to sell its brick on the local market through wholesalers but rather directly by its own directly employed sales force. A dedicated, company owned truck delivery service was also maintained at great expense. The local building material wholesalers searched for alternative sources of brick and found these in nearby Germany and Austria at prices that could more than offset the added transport costs: At the start of this research and development program a simple and manageable assessment instrument was needed to obtain systematic information about the company. The tool of choice was a SWOT - Strengths, Weaknesses, Opportunities and Threats - analysis based on a standard set of evaluation factors giving a consistent framework from which benchmark not only the company against competitors but also work progress. This tool has been chosen because it allowed, in simple terms, the collaboration of the entire workforce in assessing the situation of the company. This approach also overcame a typical problem of SWOT analyses in that they are subject to the individual priorities of the person performing the analysis and hence might have a biased focus.

At the beginning of this exercise, the following situation prevailed:

Table 34: Initial SWOT analysis

Strengths	Weaknesses
The location of the company is a point of strengths due to its accessibility by road. A further positive point is the ISO 9001:1996 certification that has been obtained; The company can benefit from extensive and wide Governmental support, in the form of grants and allowances for investments, research and development, worker training etc.	A negatively differentiated product is a major weakness as possible clients will prefer better-quality substitutes supplied mainly by foreign competitors and sold through capillary whole sales organizations; Utilization of metal surface treatment sludges; Not having been able to reduce manufacturing, and above all energy costs, as competitors means the company is outlaying more of their profits, or not generating any at all, resulting a major weakness; Old and mostly obsolete and outdated plant; R&D work is low and insignificant and this associated to old and outdated technologies and lack of industry knowledge limits success, as other firms are making use of better and more reliable technologies having better industry knowledge; Less than necessary trained staff increases maintenance costs; No cost or cash management; Lack of corporate governance and targets and goals for the company make it difficult for the stakeholders to deal or associate themselves with the company; An ineffective marketing strategy, contact to customers is through only one single sales agent and no access to distribution channels, seriously endangers the future of the company; Low production volumes and negative product image resulting in low prices placed the company in a poor financial

	position which makes it weaker than its competitors; An online presence is certainly not vital for success I the brick industry these days but helps to communicate with customers especially as far as formal certification is concerned. A lack of such a presence is a limitation; Use of metal treatment sludges.
Opportunities	Threats
Public funding for researched and development work available; Public funding for workers training available; Public funding for investments available.	Insufficient funds and profitability, insufficient financial stability; Regulations requiring money to be spent or measures to be taken could put financial or other pressure on the company; Price wars between competitors, price cuts and so on could damage revenues and rising costs could be a major downfall; Extra competition and new competitors entering the market could unsteady the market situation and be a threat.

The company did not exhibit a significant number of points of strength and hence had no edge over any competitor, except its location and the access to substantial public funding and grants for research and development work and investments, . The potential weaknesses, things that need to be improved or perform better, and threats, factors which may restrict, damage or put areas of the business or organization at risk, significantly outnumber the points of strength.

The following timed list constitutes an overview of the remedies taken and the associated industrial application of these solutions. Each point is explained in detail later in this thesis, and all are based on the research and development work of the author. These developments led to a substantial improvement in the companies trading position and also its relationship with both internal and external stakeholders, resulting in a substantial reduction in the environmental impact of the product and the production process.

- 1999:

  First tests with treated waste water sludges. The aim is to reduce the use of quarried clay and generate additional income from gate fees.

- 2000:

  The use of metal surface treatment sludges is discontinued in order to improve quality and aspect of the product;

  Utilization of paper sludge is commenced;

  An authorization for trial runs with sewage sludge has been granted by local authorities to use this waste as a brick body density reducing agent additive and clay substitute in brick making;

  Implementation of a corporate governance scheme;

  Workers training commences.

- 2001:

  A patent is filed for the waste water sludged treatment process (161).Consequently a permit for the use of sewage sludge is granted by the authorities. This creates and additional source of income improving the financial situation by reduction of the energy requirements of the ceramic process by incorporating combustible waste materials into the feedstock as body fuel and by reduction of the quantity of quarried raw materials in order to extend the service life of the quarries and reduce dependency on third party deliveries;

  Sewage sludge is used as a component in the brick feed;

  The SWEDAC EPD project is formally launched in the second half of 2001 as a is a joint project between Ziegel Gasser Mattoni GmbH S.r.l., the original promoter, ANDIL – the Italian Brick Makers Association and ANPA – Agenzia Nazionale per la Protezione dell'Ambiente, an Italian state body. Due to a reorganization, ANPA drops out of the project.

- 2002:

  Fruit processing wastes and ashes are introduced as component of brick feed;

  In collaboration between ANDIL, the Italian brick makers national association, and Ziegel Gasser Mattoni GmbH S.r.l. the very first PCR Product Category Rules now PSR Product Specific Requirements, a prerequisite for EPD, for clay masonry units has been developed and published by SWEDAC as "provisional";

  Brand building, "the only brick fired with renewable energies" starts and is publicized;

  Product cost calculation system introduced;

  First tests with a shipping container based biogas plant. The gas generated in the trials is sufficient to generate a volume of gas sufficient to power a single burner allowing testing of the effects of biogas on burners, compressors, valves and other equipment;

  Laboratory tests with renewable fuels;

  Beginning of kiln modifications.

- 2003:

  The brick plant returns to profitability;

  The hitherto used boiler oil is substituted with rendering fat as fuel for the kiln.

  On April 07, 2003 Ziegel Gasser Mattoni GmbH S.r.l. becomes the first brick manufacturer in Europe to feature an ISO compliant EPD[1] under the SWEDAC system for its products certified by RINA. This is the second in all Italy. This EPD is still based on a provisional PCR.

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[1] See later chapter on EPD as well

Fig. 38: EPD Certificate

RINA Società per azioni
Gruppo REGISTRO ITALIANO NAVALE - Via Corsica, 12
16128 Genova - Italia

CONFORMITY STATEMENT

Upon request of the interested parties and on the basis of the assessments carried out by this Certification Body, both of the documents submitted (LCA Study Rev. 5 dated 13/01/2003) and at the Organisation's premises performed starting on 28/11/2002,

WE HEREWITH STATE THAT:

The Environmental Product Declaration (EPD) Rev. 0 dated 11/03/2003
relevant to the following Product:

Masonry units, clay bricks

issued by the Organisation

ZIEGELEI GASSER MATTONAIA S.r.l.

Schabs 104 Ziegeleistr. 39040 Naz – Sciaves (BZ) - Italy

Is in compliance with the requirements of **MSR 1999:2**

In witness of the above, the Declaration has been pre-certified by RINA on 14/03/2003
The Environmental Product Declaration specified in this Statement is to be submitted to the Swedish Environmental Management Council for registration.

This Statement is issued for use as allowed by the laws in force.

RINA
Via Corsica ,12 - Genova

Date of issue, 14/03/2003

Form CERGEN - 02/00

Ziegel Gasser Mattoni GmbH S.r.l., already certified ISO 9001:1996 is certified ISO 14.001:2001 by ÖQS.

Fig. 39: ISO 14.001:1996 certificate of Ziegel Gasser Mattoni GmbH S.r.l.

ÖQS

ÖQS-ZERTIFIKAT

Die ÖQS – Zertifizierungs- und Begutachtungs GmbH stellt folgenden Organisationen ein ÖQS-Zertifikat aus:

Ziegel Mattoni Gasser

Ziegelei Gasser GmbH
I-39040 Natz, Schabs 104

Dieses ÖQS-Zertifikat bestätigt die Anwendung und Weiterentwicklung von einem wirksamen

UMWELTMANAGEMENT-SYSTEM
entsprechend den Forderungen der
ÖNORM EN ISO 14001:1996

Registrier-Nummer: 331/0
Erstausstellung: 13. Oktober 2003
Gültig bis: 8. Juli 2006

Die Gültigkeit dieses ÖQS-Zertifikates wird durch jährliche Überwachungsaudits und dreijährige Verlängerungsaudits aufrechterhalten.

Wien, am 13. Oktober 2003

ÖQS - Zertifizierungs- und Begutachtungs GmbH

TR Ing. Viktor Seitschek
Präsident

Konrad Scheiber
Geschäftsführer

Ing. Wolfgang Hackenauer
Fachbeauftragter

Laboratory test with renewable fuels;

A two stage kiln internal post combustion system is installed and put into service.

- 2004

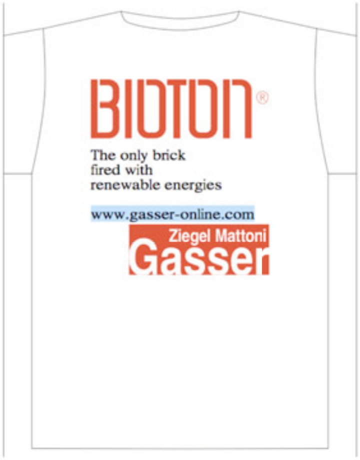
  Glass fiber cut-offs are introduced as component of the brick feed;

  A pilot plant, with a shortened methane generating cascade fashion set of vessels and hence shortened fermentation times, has been built and run with surprising results until the end of 2005 when it has been put out of service;

  New and improved burners are installed and a flue gas recycling system built.

  Plant runs exclusively on alternative / renewable fuels.

Fig. 40: T-Shirt printed to celebrate the exclusive use of renewable fuels



- 2006:

  A second EPD under the German AUB system is awarded to Ziegel Gasser Mattoni GmbH S.r.l. for its bricks.

3.3 Corporate governance

From 2000 on, Ziegel Gasser Mattoni GmbH S.r.l. has taken steps to become a good corporate citizen working hard to create good relationships with all stakeholders. The importance of documenting evidence of the efforts taken was felt to be important. For the purpose of communication with the direct stakeholders, a SA 8000[1] and OHSAS 18001 certification was originally envisaged. Both certifications were intended to be a demonstration that the working conditions at Ziegel Gasser Mattoni GmbH S.r.l., notwithstanding the use of waste materials in substitution of raw materials and alternative fuels, are safe and, maybe, even enjoyable. In the end, neither SAI nor OHSAS certification were pursued because of the small size of the company. Obtaining and maintaining this kind of certification would have been too costly and created an unsustainable overhead. It was nevertheless decided that the principles and rules of SA 8000 and OHSAS 18001 would be used either as a tool in communicating with the direct and indirect stakeholders and/or as a guideline for safety in the plant. For this purpose, a pre-certification audit, hence a full certification audit but without the goal of finally being certified, was carried out. In the course of this pre-certification audit all relevant issues related to SA 8000 and OHSAS 18001 were discussed over a three days period with the participation of the working staff.

A map of interdependencies was developed during the pre-certification audit used to visualize the interlaced effects of any action.

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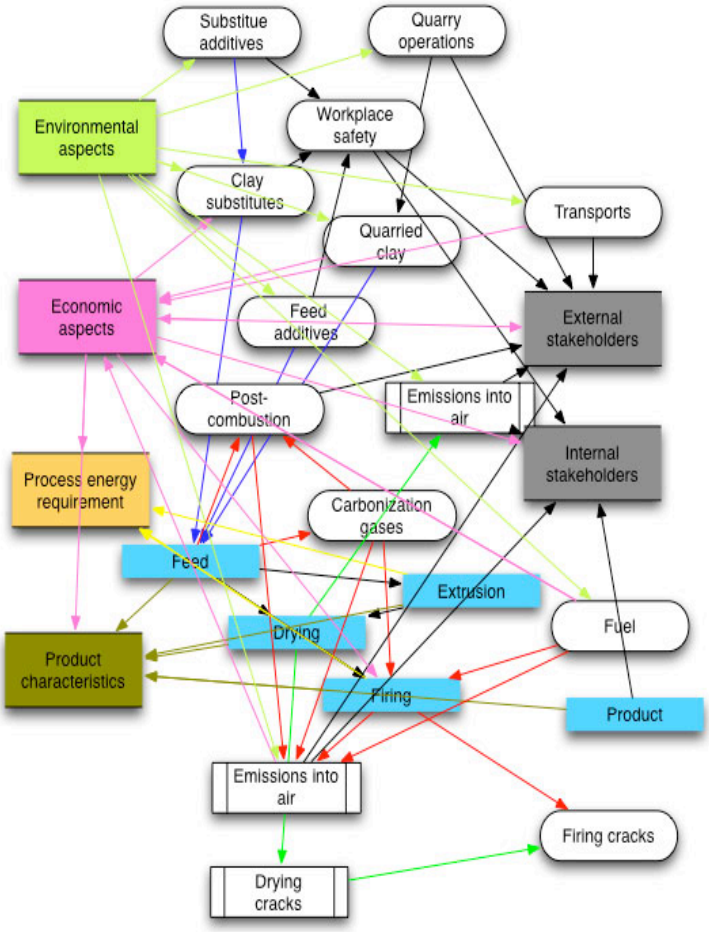
[1] The SA 8000 certification does constitute an excellent base of discussion of workers and management/owner reciprocal rights and duties.

Fig. 41: Interdependencies



The above is an abridged version of the original, dynamic model that was developed.

The single phases of the project as reported in this paper are, in most cases, a direct consequence of each other. An example: A higher percentage of organic brick body density reducing agent substances in the feed will affect:

- Mixing of the raw materials due to different densities of the materials;
- Extrusion due eventual formation of layers if the feed is not properly mixed;
- Drying cracking, and hence cracks of the finished brick, if the drying profile is not adequate to the feed and product type;
- Formation of low temperature carbonization gases that might require post combustion if the firing profile is not choose accordingly.

It can be seen that significant complexity results from the substitution, and, to a lesser extent, addition of raw materials with wastes. The lack of consideration of these interactions is also a major point lacking in many scholarly studies about utilization of waste materials in addition or substitution.

The first stakeholders to benefit from the newly adopted corporate governance scheme has been the workforce. It was felt that their skills had to be improved in order to make them better understand what, and above all why, was going on. Professional training courses, taught by by the author or by outside experts as, for example, from the IZF – Institut für Ziegelforschung, have been offered to the employees to better prepare them for their job and give them the possibility to become more accountable and take more responsibility for their work.

Workers families participation was encouraged as well by inviting these to important events such as work related anniversaries. Participation, mainly by the author, in national and international lobby activities and industrial panel work groups such ISO, TBE and ANDIL was also sought in order to rise the visibility of the company.

Building credibility with authorities and clients has also been a prime objective. This was also expressed with the SWEDAC EPD and the ISO 14.001:1996 first and later 14.001:2001 certification.

3.4 Financial aspects

The comparative cost of energy in the countries from which brick manufacturers compete in the local, South Tyrolean, market is given in Table 35:

Table 35: Comparative cost of energy[1]

Source of Energy		2000	2001	2002	2003	2004	2005	2006
A[2]	Boiler oil €/ton	222.20	209.01	212.66	256.85 198.72	237.44 214.00	307.02 284.92	405.24 334.05
	Electricity €/kWh				0.0678	0.09	0.08	0.09
D[3]	Boiler oil €/ton	207.52	194.71	197.83 160.80	219.96 173.00	203.02 163.81	237.88 231.49	334.30 283.84
	Electricity average 24 hrs €/kWh	0.100	0.1045	0.1042	0.1099	0.1134	0.1182	0.1231
I[4]	Boiler oil €/ton	233.44 293.00	229.82 250.00	223.45 232.00	270.82 257.00	253.64 255.00	314.17 334.00	397.28 385.00
	Electricity €/kWh			0.095	0.093	0.101	0.112	0.118
	Rendering fat €/ton			65.00	78.00	80.00	120.00	140.00
	Recycled frying oil €/ton							290.00
	Natural gas €/m^3[5]		0.21	0.18	0.19	0.2	0.24	0.29

Leaving aside the differences in statistical price information, boiler oil in Italy has always been more expensive (except for 2006) than in the countries from where brick is imported to South Tyrol. It should be noted that the above table does not mirror the true situation as almost all foreign competitors are using lower priced natural gas to fire their kilns, compared to the liquid fuels used at Ziegel Gasser Mattoni GmbH S.r.l.. Hence. the differences in energy related production cost are even greater than those described in the overview above.

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[1] Data in italics from EUROSTAT, partially recalculated.

[2] All data based on Austrian Statistical Office information. No statistical data are published prior to 2003 by either the Austrian Statistical Office or by EUROSTAT

[3] All data based on DESTATIS information (partially recalculated)

[4] Fossil energy prices, for comparative reasons, from Unione Petrolifera publications, Electricity and other prices from Gasser directly. Prices for boiler oil for Gasser higher than indicated by Unione Petroliera due to transport cost from refinery to Gasser plant. Transport cost on the average about 25 €/ton.

[5] Based on average prices paid by VELA S.p.A.

The cost of thermal energy per kWh for Ziegel Gasser Mattoni GmbH S.r.l. is given in the following table:

Table 36: Cost of tunnel kiln fuels for Ziegel Gasser Mattoni GmbH S.r.l.

Description	2000	2001	2002	2003	2004	2005	2006
Firing temperature in °C	940	940	760	820	820	860	880
	#6 boiler oil		#6 boiler oil rendering fat		rendering fat		rendering fat frying oil
				Flue gas recycling system			
					Purpose built burners		
						Higher firing temperatures for better mechanical strength	
t brick manufactured	19,771	17,500	18,900	18,884	19205	19,053	17,980
MJ energy consumed	45,990,000	37,741,200	33,125,400	31,840,000	27,780,400	33,332,600	34,813,820
kJ/kg brick	2326.18	2156.65	1752.66	1686.06	1446.52	1749.46	1936.22
kWh/t brick	646.16	599.07	486.85	468.35	401.81	485.96	537.84
€/kWh thermal energy used			0.0215	0.0153	0.0080	0.0086	0.0290
€ energy t/brick	n.a.	n.a.	10.47	7.16	3.21	4.17	15.59
€ energy t/brick fossil equivalent boiler oil Italy				10.55	8.82	13.09	16.51
€ energy t/brick fossil equivalent natural gas Italy		14.27	9.96	10.09	8.42	13.73	15.27

The switch from fossil to alternative fuels did not cause any increase of energy costs. If biogas generated from urban waste, see Chapter 5.4, would have been used, energy instead of generating expenses could have been a source of revenue.

The average thermal energy requirement for brick plants in Northern Europe is about 1,741 kJ/kg brick (269). More recent data for German brick plants, manufacturing more or less similar products to the ones Ziegel Gasser Mattoni GmbH S.r.l. manufactures, indicate a requirement of thermal energy of 1,575 kJ/kg for 1989 and of 1,423 kJ/kg for 2004 (270) net of electric energy. The consumptions of Ziegel Gasser Mattoni GmbH S.r.l. are hence well within the averages notwithstanding a very unfavorable kiln design. The Ziegel Gasser Mattoni GmbH S.r.l. tunnel is a vaulted kiln with a large center gap between the upper layer of brick stocked on the kiln car and the ceiling. The Ziegel Gasser Mattoni GmbH S.r.l. kiln requires a far larger degree of turbulence inside the kiln than a more modern flat ceiling kiln in order to achieve similar patterns of horizontal heat distribution and heat transfer. The total thermal dead mass of a modern tunnel kiln is also lower than that of a vaulted kiln.

With the introduction of mechanical setting of the kiln cars and the modifications to the kiln with the rebuilding as flat roof sections of the pre-heating and cooling zone it has not been any more possible to taper the bricks on the kiln car in the upper layers hence loosing a considerable volume of brick to be fired and experiencing heavy disadvantages in the circulation of hot gases and hence heat exchange. Furthermore the relative surface and mass of the kiln is much greater, resulting in a higher loss of thermal energy.

Fig. 42: Ziegel Gasser Mattoni GmbH S.r.l. vaulted roof tunnel kiln

The leftmost and central picture show the vaulted roof of the Ziegel Gasser Mattoni GmbH S.r.l. tunnel kiln (see the cross section of the Bock kiln on page 11) while the rightmost picture shows the flat roof cooling section (see page 12 for typical flat roof kiln). The gap upper layer of brick / roof in the flat roof sections is between 10 and 7 cm, depending on format of the brick and hence stacking height, whereas, in the vaulted section, it exceeds 40 cm. The wide gap between the uppermost layer of brick and the kiln roof causes hot air to flow towards the the chimney instead of contributing to an exchange of heat. This requires, in order to break the flow, burners with high combustion air exit speeds of over 150 m/s.

In order to increase circulation around the bricks some formats needed to be set in a particular, open fashion on the kiln cars. In this case “open” indicates that the bricks are set to the maximum height but that they are not set to maximum load capacity but rather with large spaces in between to allow for better circulation of the hot gases around the brick.

Fig. 43: Open setting on kiln car at Ziegel Gasser Mattoni GmbH S.r.l.

This setting resulted in a more uniform firing of the bricks.

An example of a brick not suitable for production in the Ziegel Gasser Mattoni GmbH S.r.l. kiln is shown in the following picture. A huge gap is visible between the upper layer of brick and the roof of the kiln resulting in substantial thermal losses.

Fig. 44: Bricks set at insufficient height on kiln car at Ziegel Gasser Mattoni GmbH S.r.l.

Wide gap between upper layer of brick and ceiling of kiln (in the vaulted section this will be even more pronounced)

Brick to be fired

Kiln car

The wide gap between the burner flame exit and the brick stacked on the kiln car together with the draught in the kiln made for frequent contact between the flame itself and the brick to be fired that caused spotted brick.

Fig. 45: Burner flame spotted product

The existing burners did not allow for a better quality, they were simple injection burners and hence no control whatsoever of flame shape was possible,. Compared to “spotless” products sold on the local market this was a major issue for Ziegel Gasser Mattoni GmbH S.r.l.. These spots are not necessarily an indicator of lesser mechanical qualities but certainly are an “optical” issue. No home owner would like to see a spotted wall, even if this were going to be rendered and plastered over, when a wall of even color can be obtained for the same price.

Another problem that needed to addressed was the product price structure.

The evolution of brick prices in the years following are detailed below. Bricks sold at a price lower than the cost of production are shown in red:

Table 37: Published wholesale prices for Ziegel Gasser Mattoni GmbH S.r.l. bricks in € per piece FOB Ziegel Gasser Mattoni GmbH S.r.l. plant

Brick type	2002	2003	2004	2005	2006
Doppelgitter 12/24	0.33	0.37	0.32	0.51	0.51
Blockziegel schwer Z 8	0.23	0.26	0.23	0.34	0.34
Blockziegel schwer Z 12	0.35	0.39	0.37	0.50	0.50
BIOTON Bp 12/40 N	0.51	0.58	0.51	0.69	0.69

Brick type	2002	2003	2004	2005	2006
BIOTON Bp 17/33	0.57	0.65	0.64	0.79	0.79
BIOTON Bp 20/38	0.69	0.79	0.79	0.96	0.96
BIOTON Bp 25/40 N	0.84	0.96	1.07	1.19	1.19
BIOTON Bp 30/24 N	0.70	0.80	0.81	0.90	0.90
BIOTON ECK B 30/12	0.45	0.50	0.57	0.73	0.73
BIOTON Bp 34/25 N	0.80	0.92	0.95	1.08	1.08
BIOTON ECK 34/10	0.52	0.59	0.57	0.70	0.70
BIOTON Bp 38/25 5N	0.82	0.94	1.02	1.13	1.13
BIOTON ECK Bp 38/11	0.59	0.67	0.50	0.84	0.84
BIOTON ECK Bp 38/25 E	0.82	0.94	1.09	1.08	1.08
BIOTON Bp 42/23 N	0.86	0.99	1.08	1.25	1.25
BIOTON BP 30/24 N I 0,16	0.76	0.87	1.02	1.03	1.03
BIOTON BP 34/25 N I 0,15	0.87	0.99	0.95	1.20	1.20
BIOTON BP 38/25 N I 0,14	0.89	1.02	1.02	1.25	1.25
BIOTON BP 42/23 N I 0,14	0.94	1.07	discontinued		
BIOTON BP 38/25 N I 0,12	1.05	1.09	1.08	1.41	1.41
BIOTON BP 20/38 I 0,16	new in 2005			0.96	0.96
BIOTON Bp 25/40 N I 0,17	new in 2005			1.19	1.19

Ziegel Gasser Mattoni GmbH S.r.l. experienced a very uncommon market situation:

- “Turning Green” resulted for Ziegel Gasser Mattoni GmbH S.r.l. in a more niche, willing to pay a premium for an environmentally conscious product. These “green” bricks are delivered over a distance of more than 600 km, a very uncommon practice for a generally “local” product.
- The negative quality and product image on the local market caused by delivering over years a sub-standard product in stiff competition with foreign brick of better quality and frequently lower prices could never be fully offset. Local wholesalers, through whom the product was distributed once the own expensive sales organization had been given up, placed the product, notwithstanding its intrinsic green characteristics, on a middle price and quality level. The “green” image bonus could not be put to advantage locally.

In 2001 a cost of goods sold calculation system was introduced. With the aid of this system, production costs for each single line of brick could be calculated. The result was that almost all bricks were being undersold, i.e. the sales price of the brick was lower than its production costs. Prices were being fixed in response to market requirements rather than production costs. Underselling was induced and forced poor product quality. It was however, in many cases, the only chance to sell the bricks. In 2002, 98.72% of the total tonnage manufactured was sold at a loss. With substantial improvements in quality and considerable reduction of costs resulting from the implementation of the results of the research and development work, the situation changed and the number of bricks sold at a loss was reduced. In 2003 the tonnage sold at a loss was down to 63.78% of the total tonnage produced. The per piece loss on some bricks, for example the BIOTON 12/40N that alone accounted for 16 to 17 % of the total sold tonnage, was reduced from 0.17 Cent a piece to 0.03 Cent. The higher product quality and a different marketing strategy aimed at finding new markets for the product, resulted in an average price increase of more than 11%.

The introduction of new types of brick, such as the 0.12 λ_{brick} 38 cm wall thickness brick, resulted in a substantial boost to profitability.

The overall turnover figures of the company, in themselves, might be misleading. Cross – financing of the various branches of the activity, waste recycling – sale of aggregates for concrete – ready mix concrete – sand and gravel, was common practice.

The overall, recalculated from the actual balance sheets of the company, result for 2002 and 2003 from brick production alone are given in Table 38:

Table 38: Revenues / Expenses brick production 2002 / 2003

Description	2002	2003	2003 adjusted for R&D charges co-financing
Revenues from sale of brick	900,334.00	1,192,867.59	1,192,867.59
– Σ Expenses (includes one time R&D charges)	1,286,589.72	1,198,796.00	1,198,796.00
+ Co-financing R&D charges			40,329.10
= Result	- 377,255.72	5,929.59	34,399.75

Revenues from recycling of wastes have been omitted on purpose in this table as cross-financing the loss making brick business with revenues from other activities of the company, even if closely allied, cannot be considered good practice. The total R&D charges in 2003, and for the first time such charges have been accounted for separately and not as part of the total overhead expenses, are greater than 200,000 Euro inclusive of allowable overheads and charges.

The quantities of the wastes accepted over the years have become increasingly important with better knowledge and greater skill in using them. For fruit processing wastes, delivery expenses had to be paid for, the glass fiber delivered to the brick plant did not command any gate fees. The gate fees for the other wastes delivered evolved over the years. For sewage sludge it was from 50.00 €/ton to 75.00 €/ton and for paper sludge from 20.00 €/ton to 27.50 €/ton delivered. In the years following 2004 it became prudent to reduce the volumes of paper sludge accepted because of the higher revenue generated by using the sewage sludge.

Table 39: Gate fees and quantities wastes accepted[1]

Description	2000	2001	2002	2003	2004	2005	2006
Paper sludge t	552.21	730.86	1,843.59	2,996.00	2,438.13	762.93	287.98
Fruit processing waste including ashes t	not used	not used	430.45	1,545.00	1,904.25	1,836.64	2,352.83
Sewage sludge t	not used	908.56	822.73	1,186.00	3,621.03	5,204.31	3,386.21
glass fiber cut-offs t					2,451.94	2,670.61	1,472.96
Revenue €	11,044.20	60,045.20	84,387.83	129,695.00	267,756.45	355,825.35	226,277.80

As can be easily seen, the revenue from the utilization of waste have made a substantial contribution to the brick yard's economic overall situation considering that the sale of brick covered the direct cost of production of the latter and that, hence, all income from gate fees was additional.

A necessary measure to further improve the financial situation was the reorganization of the distribution channels. In 2004 a decision to terminate the employment of the two sales agents and and hence ending direct sales in favor of selling to wholesalers was taken. At the same time the delivery and trucking business was outsourced.

In conclusion it is evident that the application of the waste and alternative energy use research and development work of the author at Ziegel Gasser Mattoni GmbH S.r.l. resulted in additional income and lower production costs. An improvement in the overall sustainability of the production process hence resulted in a considerable source of income.

3.5 Sustainability of the Ziegel Gasser Mattoni GmbH S.r.l. production process

The production process at Ziegel Gasser Mattoni GmbH S.r.l. differs from traditional brick making with the positive effect of reducing the environmental impact. When comparing processes, the differences might not appear to be substantial, but a closer look at the impacts clearly shows differently, as described in Table 40:

Table 40: Process differences

<table>
<tr><th>Description</th><th>Europe</th><th>Italy</th><th>Gasser</th></tr>
<tr><td>Raw materials</td><td colspan="2">Quarry
100 % Primary raw materials[2]</td><td>Secondary raw materials on dry matter base < 15% in weight, on wet substance base > 35% in weight. Reduced use of land due to lesser quarry activities.</td></tr>
<tr><td>Brick body density reducing substances</td><td colspan="2">brick body density reducing agent with waste styrofoam, saw dust, paper sludge, industrial sludges etc.</td><td>Brick body density reduction with selected waste water sludges, fruit processing sludges and combustion ashes, glass fibers</td></tr>
<tr><td>Fuels</td><td>Boiler oil # 5 and # 6</td><td>Boiler oil # 5 and # 6</td><td>Renewable fuels</td></tr>
</table>

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[1] Data before 2003 from accounting data, data from 2003 third party verified

[2] Raw materials are added with other substances to obtain certain characteristics but are not substituted with waste materials in the sense that they are exchanged one for the other.

Description	Europe	Italy	Gasser
	Light boiler oil Natural gas	Natural gas	
Firing temperature	> 820 °C – > 1,100 °C		< 860 °C and hence reduced fluor and chlorine emissions.
Flue gas treatment	Internal or external post combustion is mostly used in countries with a large percentage of low density blocks produced such as Germany or Austria, none in many other countries with a more "conservative" product strategy.	None - except one in operation for a short period at the RIL, today the Wienerberger, plant, in Gattinara.	Two stage internal post combustion

The environmental impacts of the Ziegel Gasser Mattoni GmbH S.r.l. production process have been certified by an EPD according to the SWEDAC system first and an EPD according to AUB in addition later[1]. The SWEDAC EPD data are used to benchmark the process against itself over time and against published data like, for example, the GBC Green Building Challenge data (271).

3.5.1 Use of Energy

The single most important reduction in the environmental and financial impact of the production process comes from the use of renewable fuels. Avoided emissions into air due to the use of renewable fuels and total fuel consumption figures are given in Table 41:

Table 41: Avoided emissions and consumptions

Description		2000	2001	2002	2003	2004	2005	2006
Consumption of fossil fuels in	MJ	45,990,000	37,741,200					
Consumption of mix fossil/renewable fuels	MJ			33,125,400	31,840,000			
Consumption of renewable fuels	MJ					27,780,400	33,332,600	34,813,820
Avoided CO_2	t[2]				817	2,089	2,506	2,302
Avoided SO_2	t[3]				931	2,381		2,624
Avoided NO_x	t[4]				414	1,053		1,166
Avoided CO	t[5]				672	1,720	2,063	1,895

The methodology of the fuel switch and its technical implications are explained in Chapter 5.

The environmental impacts of the production and use phase are given in Table 42:

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[1] Benchmarking of data between two EPD systems can be, as explained in Appendix II, misleading and result in erroneous valuations, especially if data sources for generic data are not indicated, as in the case with the GBC Green Building Challenge data.

[2] CO_2 declaration EC 2003/87

[3] CO_2 declaration EC 2003/87

[4] 1,6 g NO_x kg fuel – IPPC directive

[5] 2,6 g CO kg fuel – IPPC directive

Table 42: Impacts 2003

Impact category	Unit	Production	Use
Global Warming Potential GWP_{100}	kg CO_2 eq. /t	64.83	16.890
Stratospheric ozone depletion	kg CFC_{11} eq. /t		
Acidification	kmol H^+ eq. /t	0.040	0.01
Photochemical ozone creation	kg C_2H_4 eq. /t	0.8	0.08
Eutrophication	kg O_2 eq. /t	26.70	0.96

The GBC-study of the clay brick industry in Germany, Austria and Switzerland indicates a GWP100 of 194,000 g CO_2 eq./t. The Ziegel Gasser Mattoni GmbH S.r.l. bricks value is about 1/3 of the value of brick fired with fossil fuels.

For the year 2006, in which only renewable fuel has been used, the environmental impact data are given in Table 43:

Table 43: Impacts 2006

Impact category	Unit	Production	Use
Global Warming Potential GWP_{100}	kg CO_2 eq. /t	120.7	20,000
Stratospheric ozone depletion	kg CFC_{11} eq. /t	304.5	
Acidification	kmol H^+ eq. /t	0.107	
Photochemical ozone creation	g C_2H_4 eq. /t	0.085	0.047
Eutrophication	kg O_2 eq. /t	18.71	1.31

The relatively high 2006 GWP values are because almost 70% of the Ziegel Gasser Mattoni GmbH S.r.l. production was sold to distant customers, some over 600 km away, hence increasing the calculated impact from transport.

For the year 2006, in which only renewable fuels were used, the total energy content of non-renewable resources dropped from the 3,005 MJ/t to 1,502 MJ/t of electricity, due to the installation of more efficient motors, is down to 148.9 MJ/t from 333 MJ/t.

Table 44: Energy content of building materials

Description	Bulk density kg/m^3	Energy content MJ/m^3
Brick fired with renewable fuels	700	1,155.63
Brick fired with fossil fuels	700	2,265.20
Reinforced concrete[1]	2,400	5,264,90
EPS	20	1,928.00
Rockwool	80	1,399,40

The brick fired with renewable fuels features the lowest energy content of all building products available on the market today.

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[1] From the GBC handbook

The emission concentrations for the brickyard running on renewable fuels are among the lowest in the sector.

Table 45: Emission into air values 2002 / 2006 at 18% oxygen

Description	Unit	Industry		2002	2004	2005	2006
		Min	Max				
Dust	mg/Nm^3	1	30	5.00	2.63	< 0.05	2.63
NO_x as NO_2		10	550	n.a.	22.0	< 1	< 1
SO_x as SO_2		10	200	200.00	4.53	8	8
Fluoride as HF		1	120	20.00	0.28	< 0.02	< 0.05
Chloride as HCl		1	20	50.00	4.04	< 0.05	< 0.02
Total organic		50	250	n.a.	Not measurable		
Ethanol average	mg/kg brick	3,1		n.a.	μg < 0,01		
Benzene	mg/Nm^3	1	65				
Methanol average	mg/kg brick	5,7					
Phenol	mg/Nm^3	5	100				
Formaldehyde		1	20				
Aldehyde (S C1 – C4)		1	180				
Carbon monoxide	mg/Nm^3	> 300	< 1.500	n.a.	78.52	< 1	8
Mass flow	Nm^3/min			375	850 – 1,200		
Temperature	°C			125	225 - 250		
Toxic equivalent I-TEF	ng I-TEQ/m^3			0.095	0.004 -> < 0.0005		

The 2002 emission values are based on the use of #6 low sulfur boiler oil as sole fuel. From 2004 on the brick yard was operating only on renewable fuels. The reduction in emissions documents the technical progress in combustion technology, firing cycles and choice of fuels that has taken place at Ziegel Gasser Mattoni GmbH S.r.l. as a consequence of the research.

In the brick industry it is not common to test flue gases for dioxin and furan concentrations. No industry comparison data are hence published or available. It has been decided to benchmark the Ziegel Gasser Mattoni GmbH S.r.l. data against the mission limits set for for a modern and well operated waste incineration plant. These are 0.022 ng I-TEQ/Nm^3 at 11% oxygen content in the flue gas (272). Converted to 18% oxygen one does obtain a value of 0.00798 ng I-TEQ/Nm^3 , almost twice the value Ziegel Gasser Mattoni GmbH S.r.l. has achieved after the fuel switch. The 2002 value for Ziegel Gasser Mattoni GmbH S.r.l. using boiler fuel exceeds this value. Ziegel Gasser Mattoni GmbH S.r.l. begun in 2002 to measure averaged dioxin, furan, PAH and PCB emissions. This systematic collection of data, initiated by the author as part of his research and development work at Ziegel Gasser Mattoni GmbH S.r.l., is still rather unique in the brick world. It is the only direct comparison of emissions into air of a brickyard running on fossil and on alternative fuels. Steiner and Kahr (273) have carried out some continuous dioxin emission in a brickyard in Belgium in 2002. They found, attributed by them to the semi-continuous process that they define correctly as “batch-similar”, widely varying measurements that they claim nevertheless to be < 0.1 ng/m^3. A paper by Conesa et al. (274) deals with the subject but is targeted specifically to the utilization of paper sludge. The 1999 UNEP dioxin and furan inventory (275) also indicates very low emission values for dioxins from both brick and cement plants.

The detailed emission data for Ziegel Gasser Mattoni GmbH S.r.l. for these categories of pollutants are listed in Table 46 below.

Table 46: Dioxin and furan emissions 2002 to 2005

Impact category	Unit	2002	2004	2005	Waste incineration benchmark
Dioxin and furan					
2,3,7,8 - TCDD	pg/m	2.3	0.5	< 0.02	
1,2,3,7,8 - PCDD		19.9	0.4	< 0.02	
1,2,3,4,7,8 - HxCDD		20.5	0.3	0.9	
1,2,3,6,7,8 - HxCDD		33.6	0.8	0.2	
1,2,3,7,8,9 - HxCDD		22.9	0.6	< 0.2	
1,2,3,4,6,7,8 - HpCDD		111	4.2	0.8	
OCDD		108	10.8	8.9	
2,3,7,8 - TCDF		7.3	9.1	0.3	
1,2,3,7,8 - PCDF		59.1	3.2	< 0.3	
2,3,4,7,8 - PCDF		74.8	3.4	< 0.3	
1,2,3,4,7,8 - HxCDF		48.4	2.5	< 0.5	
1,2,3,6,7,8 - HxCDF		73.8	1.5	< 0.5	
2,3,4,6,7,8 - HxCDF		144	2.2	< 0.5	
1,2,3,7,8,9 - HxCDF	pg/m	42.8	< 0.5	< 0.5	
1,2,3,4,6,7,8 - HpCDF		158	5.8	1.7	
1,2,3,4,7,8,9 - HpCDF		30.6	0.8	0.6	
OCDF		44.6	4.1	3.2	
Toxic equivalent I-TEF	ng I-TEQ/m^3	0.095	0.004	< 0.0005	0.00798
PAH					
Benzo[a]antracene	µg/Nm	n.a.	< 0.01	< 0.01	
Benzo[b,j,k]fluorantene		n.a.	< 0.01	< 0.01	
Benzo[a]pyrene		n.a.	< 0.01	< 0.01	
Dibenzo[a,h]antracene		n.a.	< 0 .01	< 0.01	
Σ DB[a,e;a,h,a,i;a,l]pyrene		n.a.	< 0.01	< 0.01	
Indeno[1,2,3-cd]pyrene		n.a.	< 0.01	< 0.01	
Σ PAH			< 0.01	< 0.01	

From the above data some summary conclusions can be drawn:

- Emissions into air depend on the type of fuel used and wether the kiln is equipped with a post combustion system or not;

- The proper use of organic brick body density reducing agent agents does not, if direct discharge of low temperature carbonization gases to the atmosphere are avoided, change the chemical composition of the flue gases considerably;
- Emissions of dioxin and furan need to be controlled and verified;
- The installation of the kiln internal post combustion system recycling the low temperature carbonization gases into the firing zone allows to use high organic contents at the same time safeguarding the environment and reducing specific energy consumptions considerably;
- The installation of the purpose built burners, see page 124, further reduced emissions into air.

3.5.2 Generation of wastes

Waste generation in a brick plant is usually limited with the bulk being packaging wastes such as wooden pallets and the plastic films used to sheet the bricks on the pallets. A very limited quantity of other wastes such as lubrication and hydraulic oils are generated as well.

The quantity of waste per ton of brick produced for the year 2003 is given in Table 47:

Table 47: Waste generation 2003

Impact category	Unit	Production	Use
Hazardous	kg / t	0	0
Other wastes		155	0,5

Waste generation in 2006 has, due to a new packing system required by the distributors, increased:

Table 48: Waste generation 2006

Impact category	Unit	Production	Use
Hazardous	kg / t	0.12	0.08
Other wastes		234.99	2.09

3.5.3 Use of land

Consumption of land used for quarries as a non renewable resource is a factor not yet considered *per se* in most EPD schemes although the embodied energy for winning raw materials is calculated. It is certainly not considered in the schemes under which Ziegel Gasser Mattoni GmbH S.r.l. has prepared its own EPD’s. Unfortunately, this means that the reduced impact on land generated by the use of wastes in substitution of clay is not documented and evaluated either. Nevertheless, the notion that land is neither a renewable nor an indefinitely available resource is slowly becoming common knowledge and investigated (276). Land must be looked at as a source of social, environmental and economic benefits of limited availability (277). In many cases the use of land has created new habitats and environmental conditions. The use of waste materials in substitution of traditional raw materials does have the effect on reducing the dependency of the brick making operation on quarries and pits. It also places, according to current EPD practice, the environmental burden of producing the substitute raw material on the source. The quantity of energy used in manufacturing the the brick is reduced as the use of energy required to quarry raw materials is avoided.

In addition, quarry operations these days are, in most cases, faced with very stiff external stakeholder opposition as these are commonly seen as damaging to the natural habitat and having a negative impact on biodiversity and even the local microclimate. The far larger impact of human settlements is generally not considered at the same level. Planning constraints for new quarries, as illustrated by Brodkom (278) (279), coupled with stricter environmental impact requirements, make the remaining reserves of clay in working clay pits and quarries extremely important in terms of process continuity. Raw materials are the 'life blood' of the brick industry, and the raw material deposits are a major financial and strategic factor in the operation of the brick manufacturing industry.

Restored land over exhausted clay pits can provide useful social amenities or be converted to agriculture or forestry use. A very good example on how an abandoned clay quarry can contribute to local biodiversity and improve life is the Torrile Natural Reserve (280) close to the town of Parma, Italy, built on former quarries used by the Industria Laterizi Giavarini S.p.A. brick plant. Other examples of environmentally rebuilt clay quarries can also be found in the literature (281). Both examples demonstrate that a former quarry cannot only be used as a landfill but can enrich the local environment.

3.6 The situation in 2006 - assessment and conclusion

The 2006 picture differs substantially from the one of 1999. The overall situation of the company has greatly improved, the company was in a much better condition both with respect towards its trading position and its environmental stewardship. Nevertheless, a major point of weakness was that old and mostly obsolete machinery still persists and represents a threat. However, the potential to overcome this increased as the financial situation improved, allowing for new investments. Table 49 gives an updated SWOT analysis for the year 2006:

Table 49: 2006 SWOT analysis

Strengths	Weaknesses
The location of the company is a point of strengths due to its accessibility by road. A further positive point is the ISO 9001:1996 certification that has been obtained; The company can benefit from extensive and wide Governmental support, in the form of grants, allowances, training etc.; Well trained and motivated employees are helping to drive the company; The companies strong and recognized brand reputation means people view it with respect and believe in it. Riding high in the niche market in brick making industry has helped boost the ISO 9001:2000, ISO 14001:2001 and	Old and mostly obsolete and outdated plant.

EPD certified company, and raised reputation and turnover. The companies market position is high and strong – a major strength as it is ahead of many rivals. Additional income from gate fees from waste utilization and production costs lower than the competitors helps improve the financial situation considerably; The marketing strategy, selling through a local and a nationwide sales organization has proved to be effective; Low production costs due to patented technology: Being financially strong helps deal with any problems, ride any dip in profits and out perform rivals. Product image. Company image.	
Opportunities	Threats
Expanding the production output could help raise sales and turnover.	Regulations requiring money to be spent or measures to be taken could put financial or other pressure on the company; Price wars between competitors, price cuts and so on could damage revenues and rising costs could be a major downfall; Extra competition and new competitors entering the market could unsteady the market situation and be a threat.

The extensive use of waste materials and renewable fuels resulted in a better brick products from a technical, environmental and financial point of view:

- Unvaried leaching values when compared to an clay only brick;
- Lower environmental impact due to lesser use of quarried material and fossil fuels;
- Better thermal insulation values due to micropores than a standard brick hence resulting in a lower energy requirement for heating or cooling of a finished building;
- Better sound insulation values than a brick of comparable thermal insulation values due to a higher density;
- Better heat conservation than a brick of comparable thermal insulation values;
- Additional income from gate fees;
- The use of primary raw materials has been reduced;
- Lesser energy cost due to the use of renewable fuels.

The approach taken to obtain improvement of the situation differs substantially from the classic “commercial” way of trying to improve things. It was chosen to improve product and technology rather than to pursue marketing or pricing strategies. This approach gave excellent results in a market where product is interchangeable and where sales prices are usually rather set by the market rather than by the manufacturer.

Chapter 4

A South Tyrolean Case Study: Mattoni Gasser Ziegel GmbH S.r.l.

Advances in the utilization of waste materials and energy sources in brick making

Substitution of raw materials with wastes

4.1 Introduction

The use of waste materials at a level of around 30% in volume of the total material flow, mainly in terms of the substitution of quarried raw materials, requires a systematic approach. A pre-requisite for this was to create a considerable data base of historic data, covering both product and process, in order to be able to quickly assess the effect of any change made to the mix and to the process by the introduction of wastes with the necessary degree of accuracy.

Whilst it has been possible to draft a “non waste inclusion” product standard, the same has not been possible for emissions into air because of the lack of data. Emission values have had to be benchmarked against published information, mainly the BAT/BREF reference documents and European and Italian average values. This is not a satisfactory solution because the effects on the process through changing the composition of the feed did not become evident. This shortcoming then has to be corrected in later years so that today the brickyard has a considerable database on emissions available to it as well.

The various wastes were not introduced all at the same time but rather over a period of 5 years between 1999 to 2004. The first waste to be introduced, once the use of the chromium and metal working sludges had been abandoned, was paper sludge. Parallel with the use of paper sludge, the first tests with sewage sludge were also run. In 2001 the use of sewage sludge became state of the art within the company. The inclusion percentage was then progressively increased over time. The third waste stream to be introduced was fruit processing wastes and this was followed by the glass fiber off-cuts.

However, it was of paramount importance that that no waste introduced into the brick feed should have a negative impact on the product or the production process. In the absence of any published or otherwise publically available datait was important to generate an internal benchmark. Furthermore, it was decided to investigate,only waste streams that would be available in sufficient quantities, and with appropriate characteristics, all year round.

These criteria, and the impossibility to bring wastes from outside South Tyrol (local legislation at the time prohibited “import” of wastes from other parts of Italy[1] or from other countries) limited the potential waste streams to some major sources in the region, mainly fruit producers and waste water treatment plants. This, in itself, increased the overall sustainability of this applied research work in preferentially sourcing local waste materials.

Nevertheless, this “choice” of the potentially useable wastes is more an obligation than an act of free will. The political situation in directing the eventually suitable waste streams towards one or the other end-use or disposal played an important part as well (282).

As awkward as this might seem, the approach has resulted in the obligation to find solutions to a given waste stream rather than simply switching from one source to the other

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[1] The glass fiber cut-offs used are supplied as raw material rather than as waste

4.2 Establishing an internal benchmark for the use of wastes[1]

No published benchmarks or limit values exist for additions to, or substitution of raw materials for the clay brick industry. Defining such benchmarks on a broad, industry-wide base would be very difficult and would have to take into account a great number of variables due to the diversity of clays, shales and marls used in brick making, fuels and the very different range of products being manufactured. There exist no “content specifications” for brick.

An evaluation about whether a given waste can be successfully incorporated into a given brick feed must be based on a broad set of aggregated criteria. A single analysis can feature values that are influenced by non-standard factors such as involuntary contamination or variations in the raw materials. A systematic data collection over an extended period of time, as made at Ziegel Gasser Mattoni GmbH S.r.l., allows a sufficiently accurate valuation if a new waste stream to be added to a brick feed and a determination about whether it can be considered suitable for further investigation. The year-long data collection at Ziegel Gasser Mattoni GmbH S.r.l. allowed the eventual impact of any waste inclusion to be evaluated. Laboratory and factory trial results can be compared with the database and an indication about whether such an inclusion could make sense or not can be easily found.

The developed benchmarking and baseline system has been integrated into the company's ISO 9.001and ISO 14.000 certification. When, in 2003, the EN 771-1:2003[2] specification for masonry units - Part 1: Clay masonry units substituted the national UNI 8942 brick standard, the rules for testing required by the EN standards became part of the ISO 9.001 certified procedures as well. However, the sampling and testing methods indicated in the standards could be considered insufficient because the extensive use of waste materials requires far more carefulcontrol and scrutiny in order to enable users to prepare to counter any claims eventually made by customers.

Table 50: Sampling and testing scheme for waste materials containing mixes and products [based on (283) (284) (285)]

Impact category	Raw materials	Wastes	Feed (or feeds if different types of mixes are used)	Dry	Fired
Chemical analysis; Mineralogical analysis; Calorific value	Every three month or whenever deemed necessary	Once every three month if source deemed constant. Otherwise more frequently. Especially in case of energy rich wastes used as body fuel.		Monthly	Monthly
Sieve analysis				n.d.	n.d.
DTA	At least monthly				

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[1] This chapter is based and builds on previously published papers.

[2] The EN does not specify web thicknesses or allowed percentages of voids

Impact category	Raw materials	Wastes	Feed (or feeds if different types of mixes are used)	Dry	Fired
Plasticity “Pfefferkorn”	At least daily			n.d.	n.d.
Humidity / water content	At least daily			n.d.	n.d.
Carbonate minerals	Daily				
Shrinkage	Monthly		Daily		
Firing tests (tensile strength and compressive strength under lab conditions)	Weekly				
Leaching	At least monthly on an averaged, fired, daily sample				At least monthly on an averaged daily sample
Water absorption					
Freeze / thaw					
Porosity					
Efflorescence					
Compressive or tensile strength					

The maximum limits for acceptance for wastes at Ziegel Gasser Mattoni GmbH S.r.l. are based on the principle that no waste was to be used that would cause a detrimental effect to the brick itself or significantly alter the leaching behavior of the brick. Leaching behavior can be influenced by modifications to the firing cycle, for example, by reducing the oxygen content in the kiln atmosphere. A first step was to establish a “baseline” from which to proceed. For this purpose, products with no wastes added have been manufactured and tested. Tables 51, leaching concentrations of fired brick, and 52, content of unfired brick, are based on the results of 16 analysis performed between summer 2000 and late spring 2001. The threshold vales are further integrated with analysis made on brick from competing companies and the literature data covering the effects of leached substances to renders and plasters.

The following empirical leaching threshold values have hence been established for Ziegel Gasser Mattoni GmbH S.r.l.:

Table 51: Gasser leaching benchmark fired brick

Impact category		2000 / 2001 averages	2000 / 2001 max. values	2000 / 2001 min. values	Established threshold values
Fluoride Fl	mg/l	1.86	3.50	0.50	< 2.00
Chloride		4.08	12.00	2.00	< 20.00
Nitrate		1.00	1.00	1.00	< 5.00
Sulphate		177.92	250.00	57.00	< 200.00
Arsenic As	µg/l	21.46	95.00	3.00	< 30.00
Barium Ba		11.08	19.00	5.00	< 15.00

Impact category			2000 / 2001 averages	2000 / 2001 max. values	2000 / 2001 min. values	Established threshold values
Beryllium	Be		6.00	36.00	0.50	< 15.00
Cadmium	Cd	µg/l	1.27	7.00	0.50	< 2.50
Cobalt	Co		1.54	8.00	1.00	< 2.50
Σ Chromium	Cr		293.15	700.00	32.00	< 300.00
Mercury	Hg		0.10	0.20	0.10	< 10.00
Nickel	Ni		2.31	8.00	1.00	< 25.00
Lead	Pb		3.31	27.00	1.00	< 10.00
Copper	Cu		3.69	16.00	1.00	< 10.00
Selenium	Se		7.31	52.00	3.00	< 15.00
Vanadium	VN		83.77	240.00	10.00	< 250.00
Zinc	Zn		5.38	30.00	1.00	< 30.00

The content benchmark dates are indicated in the following Table 52. The values are benchmarked against the Gasser threshold values:

Table 52: Gasser content benchmark fired brick

Impact category			2000 / 2001 averages	2000 / 2001 max. values	2000 / 2001 min. values	Established threshold values
Oxides						
Aluminum oxide	Al_2O_3	mg/kg dry matter	15.61	18.59	13.50	< 25.00
Sulfur trioxide	SO_3		0.60	1.10	0.10	< 5.00
Antimony oxide	Sb_2O_3		1.02	1.20	0.80	< 5.00
Barium oxides	BaO		622.73	750.00	120.00	< 1,000. 00
Boron trioxide	B_2O_3		161.22	600.00	25.00	< 500.00
Calcium Oxide	CaO		11.39	16.10	5.60	< 10.00
Iron oxide	Fe_2O_3		6.71	7.50	6.00	< 10.00
Phosphorus Pentox.	P_2O_5		0.38	0.59	0.27	< 0.50
Magnesium oxide	MgO		3.7	4.70	2.50	< 5.00
Manganous oxide	MnO		0.10	0.12	0.10	< 0.25
Lead oxide	PbO		147.42	380.00	66.00	< 150.00
Potassium oxide	K_2O		2.96	3.53	2.70	< 25.00
Silica	SiO_2		45.90	53.12	40.30	< 65.00
Sodium oxide	Na_2O		1.21	1.70	0.77	< 1.50
Titanium dioxide	TiO_2		8,587.27	11,000.00	7,660.00	< 15,000.00
Zinc oxide	ZnO		293.45	360.00	174.00	< 1,000.00
Zirconium oxide	ZrO_2		318.27	390.00	250.00	< 450.00

Impact category			2000 / 2001 averages	2000 / 2001 max. values	2000 / 2001 min. values	Established threshold values
Heavy metals						
Arsenic	As	mg/kg dry matter				< 100.00
Cadmium	Cd	mg/kg dry substance	23.84	30.00	18.00	< 50.00
Σ Chromium	Cr		0.82	1.00	0.50	< 1.50
Mercury	Hg		143.18	230.00	103.00	< 200.00
Nickel	Ni		1.23	2.00	0.50	< 2.00
Copper	Cu		77.27	97.00	63.00	< 100.00
Selenium	Se		45.09	58.00	34.00	< 500.00
Lead	Pb		1.47	1.47	0.50	< 2.00
Zinc	Zn		n.d.			< 20.00
Other						
Chlorate		mg/kg dry substance	52.18	100.00	10.00	< 100.00
Fluorite						< 100.00
Material and Product						
Humidity	H_2O	mg/kg dry matter				< 25.00
Acidity		pH				4. 5 – 7.2
Conductivity		ɱSiemens				
Dry substance		%				
Not combusted		mg/kg dry matter				
Fineness		Grain size distribution				No negative impacts
Plasticity						No negative impacts
Odor (on drying)		Olfactory				No negative impacts
Firing color		Visual				No negative impacts
Shrinkage (drying – firing)		%				4.5 – 5.5
Cracking (drying – firing)						No negative impacts
Evaluation of risks and effects						
Evaluation of possible effects on the process and the product						No negative impacts
Evaluation of possible emissions						No negative impacts
Evaluation of possible health risks						No negative impacts

Impact category			2000 / 2001 averages	2000 / 2001 max. values	2000 / 2001 min. values	Established threshold values
	Evaluation of possible financial benefits					No negative impacts, preferred positive impacts
	Evaluation of possible liability risks					No negative impacts

A baseline for the mineral composition of the feed was not established.

It is traditional believe that bricks are safe to recycle if not contaminated with other materials such as mortar and rendering. Currently within the EC no laws or regulations exist that establish limits to the substances contained in or concentrations leached from a brick. Leaching limit values however do exist for the recycling of demolition materials. It is hence correct to assume that these limit concentration are the maximum limits for leaching of brick. Sooner or later the bricks are going to be recycled as a consequence of demolition of the building they are used in. In Germany, should the limit leaching values for recycled building materials currently under discussion be accepted, brick might even become a “special waste” (286). The new ordinance for the recycling of mineral based demolishing materials would exclude brick from being a recyclable material due to its natural vanadium and chromium concentrations already exceeding the legal threshold values.

4.3 Selected wastes

As described in the previous chapter, the safe use of waste products in substitution or addition to traditional raw materials requires careful planning and accurate supervision. In the Ziegel Gasser Mattoni GmbH S.r.l. brick plant the byproducts of choice are indicated in Table 53:

Table 53: Wastes in use

Type	Use
Sewage sludge	Sewage sludge has been chosen because of its high organic, extremely fine organic content and his high silica content. The finely distributed organic content allows for a so called micro-poring of the brick body and hence very good thermal characteristics of the brick itself
Fruit combustion ash	Fruit combustion ashes act as a filler and dry shrinkage reducing agent. They do feature a low organic content that on firing burns leaving small pores in the brick body. The relatively low, when compared to sand, fluxing temperature of the ashes and their fine grain makes that these, contrary to sand, bind well with the ceramic body hence not having the negative effect on compressive strength that is sometimes to be found when using sand of any origin or size.
Fruit juice filtration waste	The remaining organic content makes that they ashes also do have a very high organic contents and complement the use of sewage sludge as a brick body density reducing agent agent in the brick. In addition to this they also do posses the characteristic of quickly ferment and hence generate alcohols that considerably reduce the power requirement of extrusion. The sugars contained on combustion leave micro-pores;
Glass fiber cut off’s	Glass fiber production cut offs reduce dry shrinkage by about 1/3 compared to a clay body with no addition of fibers without reducing the compressive strength in any way. The also

Type	Use
	allow to lower the firing temperature by acting as a flux by about 75 to 100 °C when compared to a brick body without glass fibers.

The design of the mix has been significantly changed over the years. The use of glass fiber resulted in a greatly reduced level of dry breakage. The sewage sludge itself, principally the additives used in its treatment, contributed to a more plastic mass on extrusion, hence reducing the need to source as much plastic clay. Once fruit wastes had been introduced the percentage of plastic clay was further diminished. The alcohol generated by fermentation of the fruit processing wastes aided as well. Alcohols are a well known plasticizing agent in ceramics. The fluxing effect of the ashes was a further welcome effect.

The use of wastes did not remain constant over the years but experienced substantial changes, some of which were due to financial reasons (substitution of paper sludge with sewage sludge to due higher gate fees and hence higher income for the brick yard).

Table 54: Overview waste streams 2000 - 2006

	Year 2000	Year 2001	Year 2002	Year 2003	Year 2004	Year 2005	Year 2006
Paper sludge t/year	552.21	730.86	1,843.59	2,996.00	2,438.13	762.93	287.98
Fruit processing waste including ashes t/year			430.45	1,545.00	1,904.25	1,836.64	2,352.83
Sewage sludge t/year		908.56	822.73	1,186.00	3,621.03	5,204.31	3,386.21
Glass fiber cut-offs t/year					2,451.94	2,670.61	1,472.96

Whereas the waste utilization ratio is:

Table 55: Overview waste utilization ratio

	Year 2000	Year 2001	Year 2002	Year 2003	Year 2004	Year 2005	Year 2006
Total waste stream t/year	552.21	1,639.42	3,096.77	5,727.00	10,415.35	10,474.49	7,499.98
Brick manufactured t/year	19,771.00	17,500.00	18,900.00	18,884.00	19,205.00	19,053.00	17,980.00
Average material density of fired brick in kg/l	1.7000	1.7000	1.5500	1.5000	1.4750	1.4750	1.4900
Average loss on ignition in % weight loss green/fired	2.86	2.86	11.43	14.29	15.71	15.71	14.86
Average humidity on extrusion in % H2O	22.50	22.50	22.50	22.50	22.50	22.50	22.50
Total raw materials t/year	26,487.46	23,444.98	28,605.41	29,872.99	31,083.24	30,837.23	28,702.39

The average material density indicated is calculated statistically and based on number of pieces of a given product produced and the unit weight of each piece.

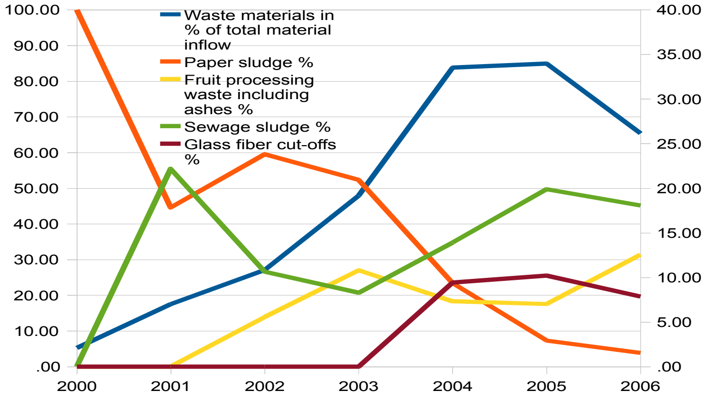
The annual waste flows are:

Table 56: Relative waste flows

	Year 2000	Year 2001	Year 2002	Year 2003	Year 2004	Year 2005	Year 2006
Waste materials in % of total material inflow	2.08	6.99	10.83	19.17	33.51	33.97	26.13
	of which						
Paper sludge %	100.00	44.58	59.53	52.31	23.41	7.28	3.84
Fruit processing waste including ashes %			13.90	26.98	18.28	17.53	31.37
Sewage sludge %		55.42	26.57	20.71	34.77	49.69	45.15
Glass fiber cut-offs%					23.54	25.50	19.64

The relative waste flows between the years 2000-2006 as a plot are as follows:

Fig. 46: Plotted specific and total waste utilization ratios



The usage ratio of wastes has steadily increased over the years. The decrease in 2006 is due to a reduced availability of glass fiber, a drop of almost 1,200 ton/year due to changes in the production process of the waste supplier, an increase in the use of fruit processing wastes and a decrease in the use of the sewage sludges (again, thorugh reduced availability). As a consequence of these changes, the average product density over the corresponding period increased slightly from 1.475 to 1.490 although this remained well within product tolerances.

It is encouraging to note that the evolution in the mix design did not result in any major changes in the chemical composition or the leachate values.

In the years 2002 and 2005 an extensive comparative verification of the chemical composition of the brick feed at Ziegel Gasser Mattoni GmbH S.r.l. was made. This comparative verification was deemed necessary to verify the efficiency of the stockpile and mixing process put in place:

Table 57: Gasser brick feed 2002 / 2005

Impact category		2000 to 2001 averages	2002 average	2005 average	Established threshold values	2000 to 2005 max values	2000 to 2005 min values	2000 to 2005 standard deviation
Oxides								
Aluminum oxide Al_2O_3	mg/kg dry matter	15.61	13.96	13.6	< 25.00	15.1	12.80	0.69
Sulfur trioxide SO_3	mg/kg dry matter	0.6	0.26	0.42	< 5.00	0.50	0.10	0.12
Antimony oxide Sb_2O_3		1.02	1.2	2	< 5.00	5.00	1.00	1.58
Barium oxides BaO		622.73	518	738	< 1,000. 00	900.00	440.00	182.62
Boron trioxide B_2O_3		161.22	61	3180	< 500.00	4,600.00	4.00	n.d.
Calcium Oxide CaO		11.39	10.56	8.24	< 10.00	12.80	7.20	1.64
Iron oxide Fe_2O_3		6.71	6.26	6	< 10.00	7.30	5.70	0.47
Phosphorus Pentox P_2O_5		0.38	0.28	0.64	< 0.50	0.90	0.23	0.22
Magnesium oxide MgO		3.7	2.54	2.28	< 5.00	2.80	2.20	0.21
Manganous oxide MnO		0.1	0.09	0.11	< 0.25	0.12	0.08	0.01
Lead oxide PbO		147.42	65	45.8	< 150.00	78.00	36.00	16.02
Potassium oxide K_2O		2.96	2.56	2.6	< 25.00	3.00	2.40	0.20
Silica SiO_2		45.9	41.78	47.4	< 65.00	49.10	37.20	3.73
Sodium oxide Na_2O		1.21	0.88	1.22	< 1.50	1.50	0.70	0.24
Titanium dioxide TiO_2		8587.27	8700	8466.67	< 15,000.00	11,500.00	6,200.00	1,515.10
Zinc oxide ZnO		293.45	163.4	163	< 1,000.00	185.00	145.00	11.06
Zirconium oxide ZrO_2		318.27	275.8	300	< 450.00	330.00	260.00	23.89
Heavy metals								
Arsenic As	mg/kg dry matter	23.84	19	16.6	< 50.00	23.00	15.00	2.49
Cadmium Cd		0.82	1.5	<1	< 1.50	2.00	1.00	0.71
Σ Chromium Cr		143.18	128.4	114.8	< 200.00	150.00	99.00	17.08
Mercury Hg		1.23	1	<1	< 2.00	1.00	1.00	
Nickel Ni		77.27	73.8	67.4	< 100.00	90.00	63.00	8.90
Copper Cu		45.09	36	37.2	< 500.00	40.00	34.00	1.96
Selenium Se		1.47	<2	<1	< 2.00			
Lead Pb		n.d.	n.d.	n.d.	< 20.00			
Zinc Zn		n.d.	n.d.	n.d.	< 1.00			

The 2002 to 2005 values are based on 5 analysis made during each year.The above data demonstrate that careful use and choice of primary and secondary raw materials in brick making does not need to significantly alter the composition of the raw material.

Maintaining such a stable overall chemical composition over the years is a major achievement considering the varying source of the clays, some are bought from outside, and the improbabilities of the composition of the wastes themselves. This has been achieved by creating stockpiles sufficiently large to cover almost one year of production and my managing the building and recovery of these well and carefully.

The leaching behavior between a waste added brick and non waste added brick is also very similar:

Table 58: Ziegel Gasser Mattoni GmbH S.r.l. leaching benchmark fired brick

Impact category		Averages 2000 / 2001	Average 2002	Established threshold values
Fluoride	mg/l	1.86	1.8	< 2.00
Chloride		4.08	5.67	< 20.00
Nitrate		1.00	< 1	< 5.00
Sulphate		177.92	195	< 200.00
Arsenic As	μg/l	21.46	10	< 30.00
Barium Ba		11.08	10.17	< 15.00
Beryllium Be		6.00	36	< 15.00
Cadmium Cd		1.27	7	< 2.50
Cobalt Co		1.54	8	< 2.50
Σ Chromium Cr		293.15	273.67	< 300.00
Mercury Hg		0.10	0.15	< 10.00
Nickel Ni		2.31	3	< 25.00
Lead Pb		3.31	27	< 10.00
Copper Cu		3.69	4.4	< 10.00
Selenium Se		7.31	52	< 15.00
Vanadium Vn		83.77	66.67	< 250.00
Zinc ,Zn		5.38	3.83	< 30.00

For 2005, based on the raw material analysis results, no leaching test were deemed necessary. The results would certainly not have been different from the data of the previous years considering the consistency and similarity in the chemical composition.

4.4 Sewage sludge

The sewage sludge research work carried out by and described here has received public funding by a research grant[1].

In order to be able to utilize sewage sludge, a treatment to avoid the generation of nauseous odors is necessary and had to be developed. A patent by the Bergakademie Freiberg suggests the use of lignite (287) as odor inhibiting agent. The use of lignite or

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[1] Massnahmen zur Förderung der Forschung und Entwicklung LG vom 13.2.1997, Nr. 4 Autonome Provinz Bozen Südtirol

coal as an odor inhibiting agent was not feasible at the outset al.tough later tests at Recuperi Industriali mixing biomass and coal combustion ashes with sewage sludge confirm the original idea of the patent. The basic idea behind the Ziegel Gasser Mattoni GmbH S.r.l. approach was that the odor treatment would have had to be made at the outset with reagents supplied by Ziegel Gasser Mattoni GmbH S.r.l..

Less interesting is the approach described in a patent by KHD Kloeckner Humbold Deutz using gypsum (288). The use of the latter would certainly cause efflorescence. The same risk applies during the common practice of using quick lime in stabilization and odor control of sewage sludge (289). Odor generation potential, from the author's experience, varies greatly from one treatment plant to the other and is also seasonal. Odor intensity is mostly non – objective. For a large number of compounds, empirical concentration threshold values are available. The masking or abolition of one odorous substance in the air might lead to the perception of another that was previously masked. The substances that generate odor are anaerobic or aerobic digestion products of mostly proteins, amino acids and carbohydrates. The odorous volatile compounds identifiable are ammonia , organic and inorganic sulfur H_2S in the form of mercaptans (thioalcohols), aldehydes, fatty acids, amines and aromatic hydrocarbons (290, 291, 292).

The novel treatment process developed and later patented (161) is primarily intended not to overcome or mask odor but rather to eliminate it by effectively stopping any bacteriological process causing it. The developed method has been subjected to a comparative study on odor treatment of paper sludge by the IZF Institut für Ziegelfoschung (Appendix VI - Untersuchung zur Gersuchsminderung beim Einsatz von Papierfangstoff) and found to be the only one that guaranteed a substantial reduction of noxious smells. Such an approach can, of course, not be taken if the sewage is intended to be landfilled or used as a fertilizer in agriculture. The developed solution is based on one short term and one long term effect additive. In order to halt bacteria growth and provide in the fresh sewage sludge benzalkonium chloride (alkyldimethylbenzylammonium chloride), preferably a C12-C14 alkyl derivative, is used. This substance is known for its strong biocide action and for being a cationic surfactant (and hence aiding in extrusion).

The use of sewage sludge in substitution and addition to classic brick making materials has been found to reduce the requirement of natural quarried raw materials and primary energy, improves extrusion and drying characteristics and generates additional income. Both the financial and the environmental impact changes are measurable.

The utilization of sewage sludge on an experimental level begun in 2000. In February 2001 a full report quoting all test results was submitted to the local authorities together with a request for authorization for the use of such sludges. This authorization was granted.

The tests, made on Ziegel Gasser Mattoni GmbH S.r.l. type Bioton B 12/40 N and Z 12 brick types, not only considered the technical aspects of the inclusion but also worker and workplace safety. The trials included testing according to the Italian Work Place Safety Regulations of the workplace environment for a range of potentially dangerous substances. Up to this point no tests sucha s these had ever been published. Comparative testing only went so far as to assess the health risk of powders generated when cutting or grinding fired bricks (see Appendix II page161).

Three production tests with dewatered sewage sludge and one with dried sewage sludge were run. The first feasibility test was run with 2.5 tons of dehydrated sewage sludge.

Table 59: Preliminary test using sewage sludge during 2000

	Density kg/l	Weight t	Volume m^3	H_2O %	H_2O t	% weight as is	% volume as is
Dewatered sewage sludge cake	1.00	2.95	2.95	85.00	2.5	13.11	17.61
Marl clay	1.32						
Plastic clay Vicenza (supplied)	1.46	19.42	13.30	12.50	2.43	86.46	79.55
Dry clay (recycled dried brick)	0.10	0.10	0.48	-0.57		0.42	2.84
Perlite as a flux	0.08						

Average density kg/l	Total weight t	Total Volume m^3	Average H_2O %	Total H_2O t
1.34	22.46	16.72	21.95	4.93

Reactants, such as the perlite used as a fluxing agent, are not included in the mass calculation.

The marl clay could not be used in this test because of a high humidity level that, in addition to the humidity added by the sludge, would have impeded mechanical handling of the extruded clay body.

A first production run was made with the following admixture:

Table 60: Test 1 - October 16, 2000

	Density kg/l	Weight t	Volume m^3	H_2O %	H_2O t	% weight as is	% volume as is
Dewatered sewage sludge cake	1.00	9.69	9.69	85.00	8.24	14.55	18.38
Marl clay	1.32	18.81	14.25	30.00	5.64	28.28	27.03
Plastic clay Vicenza (supplied)	1.46	29.13	19.95	12.50	3.64	43.75	37.84
Perlite 0-1 mm	0.08	0.15	0.95	0.91		0.23	1.80
Perlite mix as a flux	0.01	0.06					0.54

Average density kg/l	Total weight t	Total Volume m^3	Average H_2O %	Total H_2O t
1.26	66.58	52.73	26.71	17.78

The perlite mix as a flux used in this trial is a mix of perlite, borate, potash, gelatin and water glass.

The tonnage used here was sufficient to load the Ziegel Gasser Mattoni GmbH S.r.l. tunnel kiln up to 50% of its capacity. This was deemed the minimum quantity necessary for a significant flue gas sampling. It would have been better to reduce the quantity of plastic clay in order to diminish shrinkage and formation of drying cracks but in the interest of obtaining comparable results this was not done.

The flue gas data of table Table 63: was obtained with the mixes described in Tables 61 to 63. When comparing the later emission data it can be seen that th use of the flux did not have any measurable influence on the emissions into air. It would have been interesting to investigate this aspect further, but research into the use of high priced fluxes had to be curtailed for financial reasons, a production using such materials would have been financially not sustainable.

The second production run took place with a modified admixture to which paper sludge was added to reduce cracking of the green brick.
This change was dictated by the availability of the raw materials and additives:

Table 61: Test 2 - November 6, 2000

	Density kg/l	Weight t	Volume m^3	H_2O %	H_2O t	% weight as is	% volume as is
Paper sludge	0.72	1.37	1.90	60.00	0.82	1.79	3.01
Dewatered sewage sludge cake	1.00	8.55	8.55	85.00	7.72	11.19	13.53
Marl clay	1.32	25.08	19.00	30.00	7.52	32.83	30.08
Plastic clay Vicenza (supplied)	1.46	27.74	19.00	12.50	3.47	36.31	30.08
Perlite 0-1 mm	0.08	0.49	2.85	2.74		0.60	4.51
Perlite mix as a flux	0.01	0.10	0.48			0.12	0.75

Average density kg/l	Total weight t	Total Volume m^3	Average H_2O %	Total H_2O t
1.21	76.40	63.16	25.51	19.49

A third production run was made with a further modified admixture. Tho this mixture no flux was, in order to obtain a result that from a production point of view would be sustainable, was added.

Table 62: Test 3 - December 13, 2000

	Density kg/l	Weight t	Volume m^3	H_2O %	H_2O t	% weight as is	% volume as is
Paper sludge	0.93	1.80	1.92	52.10	0.94	2.85	3.63
Dewatered sewage sludge cake	1.00	3.00	8.55	71.00	2.13	4.75	5.65

Marl clay	0.80	30.50	22.88	24.50	7.47	12.66	18.84
Plastic clay Vicenza (supplied)	1.33	30.55	22.88	24.50	7.47	48.27	43.10
Perlite 0-1 mm							
Perlite as a flux							

Average density kg/l	Total weight t	Total Volume m^3	Average H_2O %	Total H_2O t
1.21	76.40	63.16	25.51	19.49

During the October 16 test run, emissions into air during the firing cycle of the sludge amended brick in the preheating zone / sludge amended brick in the firing zone and in the firing zone / sludge amended brick in the cooling zone, were analyzed. A benchmark flue gas analysis was made as well.

The emission data for the Ziegel Gasser Mattoni GmbH S.r.l. brickyard running on renewable fuels are among the lowest in the industry and are given in Table 63:

Table 63: Emissions test vs. industry vs. later years

		Industry		2000	Heating firing	Firing cooling	2002	2004	2005	2006
		Min	Max							
Dust	mg/Nm^3	1	30	**48.00**	**58.90**	**55.50**	5.00	2.63	< 0.05	2.63
NO_x as NO_2		10	550				n.a.	22.0	< 1	< 1
SO_x as SO_2		10	200	**24.00**	**20.30**	**36.80**	200.00	4.53	8	8
Fluoride as HF		1	120	**7.70**	**7.10**	**3.80**	20.00	0.28	< 0.02	< 0.05
Chloride as HCl		1	20	**32.30**	**31.00**	**9.90**	50.00	4.04	< 0.05	< 0.02
TOC		50	250	**< 3.00**			n.a.	Not measurable		
Ethanol average	mg/kg brick									
Benzene	mg/Nm^3	1	65							
Methanol average	mg/kg brick									
Phenol	mg/Nm^3	5	100							
Formaldehyde		1	20							
Aldehyde (S C1 – C4)		1	180							
Carbon monoxide		> 300	< 1.500				n.a.	78.52	< 1	8
Mass flow	Nm^3/min						375	850 – 1,200		
Temperature	°C			**165**	**166**	**164**	125	225 - 250		
Toxic equivalent I-TEF	ng I-TEQ/m^3			**0.06**	**0.012**	**0.048**	0.095	0.004	<0.0005	

The “Heating / Firing” emissions tests have been made during test run 2.

The reported emissions are found to within the emission limits applicable to the year 2000. In 2002, another flue gas analysis indicated an extremely high concentration of SO_2 in the emissions. These were attributable to some malfunctioning burners during the test. Over the years in this study the overall emissions have been reduced to values that are far lower than the documented state of the art (48)(68).

The raw materials in use during the research period were individually analyzed and the results are given in Table 64.

Table 64: Test run 3 raw materials analysis

Impact category		Threshold value	Plastic clay Vicenza	Plastic clay Vicenza	Marl clay	Marl clay	Paper sludge	Bolzano sewage sludge
Arsenic As	% dry matter	< 50.00	16.3	9.10	36.40	9.10	1.50	9.30
Cadmium Cd		< 1.50	0.50	0.70	0.20	0.40	< 0.10	0.70
Σ Chromium Cr		< 200.00	456.00	99.30	156.00	111.80	28.70	56.60
Mercury Hg		< 2.00						
Nickel Ni		< 100.00						
Copper Cu		< 500.00	53.00	38.00	12.00	37.00	24.00	379.00
Selenium Se		< 2.00						
Lead Pb		< 20.00	172.20	99.40	15.70	72.60	< 0.10	20.90
Zinc Zn		< 1.00	164.00	178.00	105.00	191.00	168.00	489

At a later date two more laboratories performed analysis on the same materials. ples provided for this analysis did not come from the same batch of paper sludge but from different deliveries. Apparently the paper sludge is subject subject to quiet important variations in the concentrations measured. The chemical composition of paper sludge must therefore be considered to feature as an important variable – a point on which there appears to be little if any published information. More attention will need to be paid to this point in the future.

Table 65: Analysis of paper sludge from Cartiere del Garda

Impact category		Paper sludge				Average	Max	Min
Oxides		University Trento	Ecocenter					
Aluminum oxide Al_2O_3	mg/kg dry matter	4.48	5.46	6.30	5.60	5.46	6.30	4.48
Sulfur trioxide SO_3		0.16	0.15	0.10	0.20	0.15	0.20	0.10
Antimony oxide Sb_2O_3			1.20	1.20	1.20	1.20	1.20	1.20
Barium oxides BaO			20.55	1.10	40.00	20.55	40.00	1.10
Boron trioxide B_2O_3			139.50	210.00	69.00	139.50	210.00	69.00
Calcium Oxide CaO		34.57	33.06	31.10	33.50	33.06	34.57	31.10
Iron oxide Fe_2O_3		0.17	0.19	0.20	0.20	0.19	0.20	0.17
Phosphorus Pentox. P_2O_5		0.07	0.15	0.20	0.18	0.15	0.20	0.07

Impact category		Paper sludge				Average	Max	Min
Oxides		University Trento	Ecocenter					
Magnesium oxide MgO	mg/kg dry matter	0.44	0.38	0.01	0.70	0.38	0.70	0.01
Manganous oxide MnO			0.10	0.18	0.01	0.10	0.18	0.01
Lead oxide PbO			6.35	5.70	7.00	6.35	7.00	5.70
Potassium oxide K_2O		0.09	0.23	0.30	0.30	0.23	0.30	0.09
Silica SiO_2		2.80	2.77	2.80	2.70	2.77	2.80	2.70
Sodium oxide Na_2O		0.06	0.32	0.50	0.40	0.32	0.50	0.06
Titanium dioxide TiO_2			215.00	240.00	190.00	215.00	240.00	190.00
Zinc oxide ZnO			19.50	21.00	18.00	19.50	21.00	18.00
Zirconium oxide ZrO_2			165.00	170.00	160.00	165.00	170.00	160.00
Heavy metals								
Arsenic As	mg/kg dry matter		1.00	1.00	1.00	1.00	1.00	1.00
Cadmium Cd			1.35	1.70	1.00	1.35	1.70	1.00
Σ Chromium Cr			10.00	10.00	10.00	10.00	10.00	10.00
Mercury Hg			2.00	2.00	2.00	2.00	2.00	2.00
Nickel Ni			10.00	10.00	10.00	10.00	10.00	10.00
Copper Cu			13.50	13.00	14.00	13.50	14.00	13.00
Selenium Se			0.50	0.50	0.50	0.50	0.50	0.50
Other								
Chloride	mg/kg dry matter		145.00	140.00	150.00	145.00	150.00	140.00

The product analysis data are:

Table 66: Test run 3 product analysis

Impact category		Threshold value	Freshly extruded brick test 3	Unfired brick test 3	Fired brick test 3
Arsenic As	% dry matter	< 50.00	13.60	12.90	9.70
Cadmium Cd		< 1.50	0.60	0.60	0.10
Σ Chromium Cr		< 200.00	145.40	154.10	37.00
Mercury Hg		< 2.00	0.16	0.22	< 0.10
Nickel Ni		< 100.00	104.60	102.60	98.50
Copper Cu		< 500.00	57.00	63.00	21.00
Selenium Se		< 2.00			
Lead Pb		< 20.00	148.00	152.00	20.00

Impact category		Threshold value	Freshly extruded brick test 3	Unfired brick test 3	Fired brick test 3
Zinc Zn	% dry matter	< 1.00	254.00	281.00	141.00

The values are in line with the values find in the later years.

4.5 Additional testing with sewage sludges

Comparative tests were run in 2003 with sludges originating from central Italy, Bologna, and supplied by HERA S.p.A., one of the large waste water processors in the region. These tests were run as a proof of concept and also because HERA had shown interest in applying the Ziegel Gasser Mattoni GmbH S.r.l. technology at local brick plants.

The HERA tests were the first tests to be run under normal production conditions with a sewage sludge of non-local origin.

The tests did not give results indicating significant differences between the brick manufactured with the HERA sludges and Ziegel Gasser Mattoni GmbH S.r.l. standard brick manufactured during the same period. However, HERA decided to not pursue and fund the project any further. As a consequence, no leaching tests were undertaken.

Table 67: HERA results

Impact category		Limit value	HERA	Gasser feed	Average 2002 / 2005
Oxides					
Aluminum oxide Al_2O_3	mg/kg dry matter	< 25.00	12.90	12.20	13.78
Sulfur trioxide SO_3		< 5.00	0.60	44.70	0.34
Antimony oxide Sb_2O_3		< 5.00	2.90	1.00	1.60
Barium oxides BaO		< 1,000. 00	500.00	500.00	628.00
Boron trioxide B_2O_3		< 500.00	68.00	71.00	1,602.50
Calcium Oxide CaO		< 10.00	10.90	11.00	9.40
Iron oxide Fe_2O_3		< 10.00	5.30	5.50	6.13
Phosphorus Pentox. P_2O_5		< 0.50	0.51	0.28	0.46
Magnesium oxide MgO		< 5.00	2.90	3.70	2.41
Manganous oxide MnO		< 0.25	0.09	0.10	0.10
Lead oxide PbO		< 150.00	41.00	39.00	55.40
Potassium oxide K_2O		< 25.00	2.50	2.90	2.58
Silica SiO_2		< 65.00	45.70	44.70	44.59
Sodium oxide Na_2O		< 1.50	0.70	0.90	1.05
Titanium dioxide TiO_2		< 15,000.00	7.200	7.600	8,583.33
Zinc oxide ZnO		< 1,000.00	245.00	140.00	163.20
Zirconium oxide ZrO_2		< 450.00	240.00	240.00	287.90

Impact category		Limit value	HERA	Gasser feed	Average 2002 / 2005
Heavy metals					
Arsenic As	mg/kg dry matter	< 50.00	17.00	15.00	17.80
Cadmium Cd		< 1.50	1.00	2.00	1.50
Σ Chromium Cr		< 200.00	140.00	115.00	121.60
Mercury Hg		< 2.00	1.00	1.00	1.00
Nickel Ni		< 100.00	74.00	67.00	70.60
Copper Cu		< 500.00	57.00	4000	36.60
Selenium Se		< 2.00	2.00	2.00	< 1.00
Lead Pb		< 20.00			
Zinc Zn		< 100.00			

4.6 Fruit combustion ash - production

The use of this waste has largely passed unnoticed by all external stakeholders. The changes to the financial and the environmental impact are almost insignificant. From a process and product point of view, the changes are important because they affect the density, firing and drying characteristics of the product. The inclusion of the ashes reduces drying shrinkage and improves drying characteristics. The difficulties using biomass combustion ashes arise from their pozzolanic behavior when mixed to clay that makes their extrusion behavior difficult: The clay strand to be extruded stiffens and the usual method of choice, adding water, does not lead to any results. It is hence necessary to hinder or delay this behavior by either adding the ashes, as done for styrofoam for example, directly prior to extrusion or by hydrophobizing the ashes at least partially with a suitable agent. At Ziegel Gasser Mattoni GmbH S.r.l. the negative impact on extrusion behavior of the ashes has been offset by the positive impact of the fruit waste that fermented and generated alcohol (the use of alcohol as an extrusion aid is well documented).

The use of this ashes has originated from the *PROGRES EU thematic network on PROduction of new products from Glassy combustion RESidues*. Albeit the Hans Zipperle AG S.p.A. ashes are not strictly within the framework of the network, they nevertheless have been the only non experimental application of combustion products presented and investigated[1]. The particularity of these ashes is that they are a byproduct of the production of fruit concentrates. In this particular production process peels and stems are not separated from the meat prior to processing. Particular care has to be taken by the producer of the waste to remove all superficial contamination of the fruit including pesticides before it enters his production cycle. The ashes do not contain sulfur in noticeable quantities. They do, however, due to the particular combustion technology using a Swiss-

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[1] See http://ec.europa.eu/research/growth/pdf/cleantechnologies-conference/presspack-cleantechno-presentation-m-janssen-22-07.pdf for reference to the project and a photo of ash containing bricks being extruded (last accessed Jan 2009).

Combi rotary kiln and in line rotary dryer, contain about 12% of non-combusted matter that is very finely distributed. For transport, the ashes are wetted down with about 10 to 15% of water by weight. The peelings and stems combusted are about 75% apple and the rest consists of other fruits such as kiwi, peach, pear etc. No citrus fruits are processed at the plant. These tests were completed in the summer of 2002 and an authorization applied for in the autumn of the same year. This was duly granted.

In the stockpile the addition of ashes and fiberglass cut-offs prevents the formation of “compacted” nests of organic sludge in which anaerobic decomposition would normally take place.

Table 68: Ziegel Gasser Mattoni GmbH S.r.l. leaching fired brick vs. benchmark

Impact category			Threshold	20% fruit combustion ash in feedstock
Fluoride		mg/l	< 2.00	1.50
Chloride			< 200.00	9.00 - 38.00
Nitrate			< 50.00	< 1.00 - 19.00
Sulphate		µg/l	< 250.00	170.00 – 240.00
Arsenic	As		< 25.00	5.00 – 15.00
Barium	Ba		< 15.00	6.00
Berillium	Be		< 10.00	< 0.50
Cadmium	Cd		< 2.50	< 0.50 – 1.00
Cobalt	Co		< 2.50	< 1.00
Σ Chromium	Ce		< 300.00	125.00 – 460.00
Mercury	Hg		< 0.50	< 0.10
Nickel	N		< 25.00	1.00 – 5.00
Lead	Pb		< 10.00	< 1.00
Copper	Cu		< 10.00	< 1.00 – 6.00
Selenium	Se		< 10.00	< 3.00 – 5.00
Vanadium	Vn		< 250.00	55.00 – 240.00
Zinc	Zn		< 100.00	6.00 – 9.00

Although the chemical analysis indicates a relatively high zinc concentration, the leaching tests did not indicate any unusual behavior.

4.7 Glass fiber cut-offs - production

The glass fiber cut-offs utilization research work carried out by the author and described here has received public funding by a research grant[1].

The use of fiber-reinforced ceramics has hitherto been restricted to ‘higher-end’ ceramic products because of the high cost of fibers involved. However, by using non-recyclable “cut-off’s” from the glass fiber insulation materials manufacturing industry, it became cost

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[1] Massnahmen zur Förderung der Forschung und Entwicklung LG vom 13.2.1997, Nr. 4 Autonome Provinz Bozen Südtirol

effective.The clay brick manufactured with the addition of this waste achieved a lower firing temperature of 840°C in comparison with an equivalent ‘all clay’ product, which normally required a temperature of 960°C.

Fig. 47: Glass fiber is added to the *mix* (VELA S.p.A. Borgonato)

The use of glass fiber cut-off's has been mainly investigated from the point of view of reduction of shrinkage (see also page 50) , lesser concavity of the cored surface of the brick, reduced firing temperatures and improved thermal characteristics of the finished product. The shrinkage reducing effect of the glass fiber cut - off’s is useful in countering the effect of increase of shrinkage and deformation when adding sewage sludge to the feed. It further helps to reduce drying and firing cracks. On drying, the moisture difference between the interior and the outer surface of the brick to be dried generates substantial stresses: The outer, drier, part of the body tends to contract while the inner sections do not follow frequently, at least at the edges of the cored brick, exceeding the cohesive forces of the clay particles. Concavity, the depth of which in non surface machined brick can reach several millimeters, requires a larger volume of mortar in brick laying to ensure that the brick itself rests stable to the underlaying course and that loads are well distributed within the wall. It is also more difficult for the brick layer to achieve a straight wall.

The glass fiber cut-off's used are chopped down to single fibers of about 3 mm in length and result in a strong structure within the brick body due to their chaotic orientation.

By comparative tests carried out on fired specimens of different fired clay bodies of similar density manufactured in the Ziegel Gasser Mattoni GmbH S.r.l. brick plant, it has been shown that the fiber added clay body does indeed have better thermal insulation properties than a clay body of similar material density but without the added fibers (293). The fibers themselves, due to the elevated boron concentration, act as frit effectively reducing the firing temperature of the brick itself. Glass, and hence glass fiber, can make otherwise unusable clays useable (152).

The chemical analysis of the sample suggests that the addition of glass fiber does not have a significant effect on the chemical composition of the fired brick as indicated in Table 69.

Table 69: Chemical analysis fiber added bricks

Impact category			Threshold value	Day 295 in 2002 10 % of fiber in volume added to brick feed
Oxides				
Aluminum oxide	Al_2O_3	mg/ dry matter	< 25.00	18.59
Sulfur trioxide	SO_3		< 5.00	0.35
Antimony oxide	Sb_2O_3	mg/ dry matter	< 5.00	1
Barium oxides	BaO		< 1,000. 00	660
Boron trioxide	B_2O_3		< 500.00	
Calcium Oxide	CaO		< 10.00	8.9
Iron oxide	Fe_2O_3		< 10.00	6.89
Phosphorus Pentox.	P_2O_5		< 0.50	0.55
Magnesium oxide	MgO		< 5.00	3.56
Manganous oxide	MnO		< 0.25	0.11
Lead oxide	PbO		< 150.00	250
Potassium oxide	K_2O		< 25.00	3.53
Silica	SiO_2		< 65.00	53.12
Sodium oxide	Na_2O		< 1.50	0.77
Titanium dioxide	TiO_2		< 15,000.00	7900
Zinc oxide	ZnO		< 1,000.00	300
Zirconium oxide	ZrO_2		< 450.00	10
Heavy metals				
Arsenic	As	mg/ dry matter	< 50.00	30
Cadmium	Cd		< 1.50	0.5
Σ Chromium	Cr		< 200.00	130
Mercury	Hg		< 2.00	2
Nickel	Ni		< 100.00	68
Copper	Cu		< 500.00	52
Selenium	Se		< 2.00	0.5
Lead	Pb		< 20.00	
Zinc	Zn		< 100.00	
Other				
Chlorate		mg/ dry matter	< 100.00	10
Fluorite				
Evaluation of risks and effects				
Evaluation of possible effects on the				Reduces shrinkage

Impact category		Threshold value	Day 295 in 2002 10 % of fiber in volume added to brick feed
process and the product			
Evaluation of possible emissions			None
Evaluation of possible health risks			None – proper abatement equipments needs to be installed.
Evaluation of possible financial benefits			None
Evaluation of possible liability risks			None

The leaching values of the brick with glass fiber added are reported in Table 70. They show substantial differences to prior values:

Table 70: Ziegel Gasser Mattoni GmbH S.r.l. leaching fired brick vs benchmark

Impact category			Production	Day 295 2002 10 % fiber by volume in brick
Fluoride		mg/l	< 2.00	1.10 – 1.50
Chloride			< 200.00	2.00 – 3.00
Nitrate			< 50.00	1
Sulphate		µg/l	< 250.00	57.00 – 160.00
Arsenic	As		< 25.00	14.00 – 44.00
Barium	Ba		< 15.00	8.00 – 13.00
Berillium	Be		< 10.00	1
Cadmium	Cd		< 2.50	1
Cobalt	Co		< 2.50	1
Σ Chromium	Ce		< 300.00	34.00 – 36.00
Mercury	Hg		< 0.50	0.1
Nickel	N		< 25.00	2
Lead	Pb		< 10.00	1
Copper	Cu		< 10.00	1
Selenium	Se		< 10.00	3
Vanadium	Vn		< 250.00	34.00 – 190.00
Zinc	Zn		< 100.00	1.00 – 2.00

A main target to achieve was an increase in compressive strength that would allow to include a higher percentage of secondary waste materials without the product compressive strength deteriorating to unacceptable levels. Comparative compressive strength resistance tests have been carried out on two formats with 10 % by volume of glass fiber added at fired at 820°C: The increase for both cases brick types exceed 50%.

The impact on the internal stakeholders was very negative at the beginning due to minor health problems. The fibers that used are classed as non-cancerous but were nevertheless causing irritation to the respiratory channels and to the skin. Special ventilation equipment had to be installed.

4.8 Conclusion

The wastes used have required substantial changes in process parameters - not so much to the production process itself as this required only adjustments due to the changed plasticity and drying behavior of the feed - but rather to the handling of the raw materials and the mixing of the feed.

The number of wastes used increased gradually over the years. The on-site personnel had the chance to slowly adapt to the changes in process and to the new requirements. It would have been impossible to make all of the changes right from the outset

For the acceptance of the various wases and raw materials receiving platforms have been built, each waste or raw material is assigned to its receiving platform. No supplier is allowed directly to the stockpiles.

In addition, the personnel in charge of accepting the various materials have been trained to be extremely careful when unloading or accepting materials and to look out for eventual contaminants (beverage containers, plastic etc.) that eventually could cause problems in the later use of the materials. Contaminated deliveries are regularly rejected or disposed off, at the expense of the waste producer, in the appropriate way (landfill or incineration).

The numbers of single feeds increased from 2 or three, the number of clays used in the Ziegel Gasser Mattoni GmbH S.r.l. brickyard previously, to more than 10 feeds that needed to be effectively managed:

- Waste water treatment sludge from the Mühlbach treatment facility;
- Waster water treatment sludge from the Unteres Pustertal treatment facility;
- Waste water treatment sludge from the Brixen treatment facility;
- Fruit; berries used in the production of food colors, processing wastes from IPRONA AG S.p.A.;
- Fruit processing wastes from Hans Zipperle AG S.p.A.;
- Fruit processing waste incineration ash from Hans Zipperle AG S.p.A.;
- Paper sludge from Cartiere del Garda;
- Glass fibers cut-off material from ISOVER;
- Clay from own quarry top quality;
- Silt from aggregate washing;
- Clay from outside source plastic;
- Clay from outside source that specifically had a low firing temperature .

All these waste streams had to be stocked separately once received, and then mixed in the appropriate ratios with clay and stockpiled until usage. In order to obtain a homogenous mix, the various flows had to be carefully managed.

Initially wastes have been accepted without any formal contract. Currently, and learning from experience, the contracts have now grown to well over 15 pages in length.

Chapter 5

A South Tyrolean Case Study: Mattoni Gasser Ziegel GmbH S.r.l.

Advances in the utilization of waste materials and energy sources in brick making

Substitutive Fuels

5.1 Fuels

The first fired bricks have certainly been manufactured using a renewable fuel: wood. It's use today is, with a few examples where wood is used either to create a special kiln atmosphere for color effects on facing bricks and one manufacturer in France, limited mostly to developing countries. Some brick yards in Europe and the US run on landfill gas, some in Europe on recycled lubricants, some are experimenting with synthgas.

Fuels can be introduced in the brick making process in two ways:

- As “external” fuels – i.e. fuels combusted with the aid of a burner;
- As “internal”, body, fuels – i.e. fuels mixed to the clay.

In both cases fuels can be either solid or liquid. Gaseous fuels can be used only as “external” fuels, whereas any solid or liquid fuel can be used as body-fuel when added to the brick body.

An overview of the potentially interesting fuels is given in Table 71 (294):

Table 71: Potential fossil and substitutive fuels

Solid			Liquid			Gaseous		
Fossil	Renewable	Alternative	Fossil	Renewable	Alternative	Fossil	Renewable	Alternative
Petrol coke	Wood and similar	Fuel from household waste	Light boiler oil	Vegetable oil and fat	Recycled frying fat	LNG	Biogas	Biogas
Anthracite		Fuel from industrial waste	Heavy boiler oil	Rendering fat	Motor oil hydraulic oil	NG		Syngas
Coke		Dried waste water treatment sludge cake		Bio diesel	Waste fatty acids			Landfill gas Sewage gas
Coal		Dried organic sludges		Alcohol (methanol, ethanol)	Synthetic hydrocarbons			Hydrogen
				Waste glycerine from biodiesel production	Pyrolysis oil			Pyrolysis gas

The use of solid fuels, albeit known practice[1], has been discarded for the fear of generating too much ash within the kiln. This ash would eventually deposit on the product surface and in the cores and could present a potential health hazard for the user. The requirement for explosion proof conveying and firing systems, except in the case of petrol coke, was deemed to difficult to achieve.

Glycerine from the production of biodiesel can not be used as a fuel due to its very high salt content that results, from the tests carried out at Ziegel Gasser Mattoni GmbH S.r.l., in “salt glazed” bricks and eventually in damage to the refractories lining the kiln, to the burners and to the the flue gas systems.

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[1] For example, the Thermo-Murg system by Walter, a system by Lingl, one by Pearce and one by Stewart et al.

Light boiler oil and bio diesel have been excluded from the investigation for financial reasons. Recycled motor and hydraulic oil would have required building an external post combustion system for the flue gases, an unrealistic investment for the company at that time. Synthetic hydrocarbons alcohols and pyrolysis oil have been excluded due to lack of available technology. LNG and NG have been excluded due to local unavailability. Same applies for landfill and sewage gas[1] (295). Syngas from coal or other organic substances such as wood could have been an alternative worth investigating. Some brick plants in the Ruhr region in Germany have been using this coal gas as fuel until the late 1970's when NG became more attractive both from an economic and from an environmental point of view. Some wood gasification, based on technology sold by the Lingl company, was in use in the North-East of Italy until the late 70ties as well. The Boral Brick Company is running, end of 2009 / beginning of 2010, a wood gasification system at their Gleason Plant and has requested authorization to built such systems at other locations as well (296).

The fuels investigated for use at Ziegel Gasser Mattoni GmbH S.r.l. were therefore those detailed in Table 72:

Table 72: Fuels selected for further investigation

Solid			Liquid			Gaseous		
fossil	renewable	alternative	fossil	renewable	alternative	fossil	renewable	alternative
				Vegetable oil and fat	Recycled frying fat		Biogas	Biogas
				Rendering fat				
					Waste fatty acids			

For oils, fats and biogas extensive tests have been run. Ultimately, following trials and substantial modification of the burners and fuel system described later in this Chapter, the fats became the fuel of choice for Ziegel Gasser Mattoni GmbH S.r.l..

Rendering fat, mainly triglycerides, compares favorably to boiler oil in emission and firing behavior. It is a non standardized fuel with varying characteristics obtained in a well known and pretty much standardized process (297). Sodium concentration, acidity (298)[2] and bacterial content is of great importance. A further important factor is viscosity and flash point of the fat that requires heat it to temperatures of 75°C and 85°C for appropriate viscosity. Severe corrosion, due to an aldehyde reaction with exposed metal surfaces, was initially found to reduce the wear-life of the pumps and injection systems conveying the tallow to only a few days. As main fuel pumps hence positive displacement pumps stemming from the food industry have been installed. All piping is manufactured of mild steel.

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[1] Jenkins in Moody, IL, Boral Brick in Terres Hautes, IL, and Union City, OK, all USA, and Olfry in Vechta in Germany run at least partially on landfill gas.

[2] The total content of fatty acids in rendering fat averages 56.8 % for saturated and 44.7% in weight for unsaturated.

In 2003, Haessler obtained a very summary patent (299) for the general use of rendering fat as fuel for a brick kiln but apparently has never carried out practical or laboratory scale trials.

One aspect not usually considered is the risk associated to the use of alternative fuels. The impact on refractories and kiln furnitures is rarely investigated. For example, the use of petrol coke, in a tunnel kiln operated by SBBC has lead, as experienced by the author, to an extensive damage of the kiln ceiling. In order to obtain reasonable combustion of the air pressure injected micronized petrol coke the kiln had to be kept in low pressure. This resulted in leakage of the kiln atmosphere into the suspended ceiling and to corrosion of the suspenders. About 80 linear meters of suspended ceiling dropped down and had to be replaced. The brick industry, unlike the cement industry (300) (301), has surprisingly not addressed the question of vanadium swelling and consequent damage to refractories up until now in any exhaustive or scholarly manner.

5.2 Modifications to the kiln and the brick dryer

The first tests with alternative fuels, namely biogas and rendering fat, began in 2002. In 2003 the previously used boiler oil was substituted, first in part and then in full, with rendering fat. The switch from fossil to substitutive fuels was completed in 2004. The difficulties encountered required substantial modifications to the firing system including the development of new burners. It was decided at the outset to built a dual fuel system that would allow the concurrent use of a liquid and a gaseous fuel. Such burners were not available on the market and therefore these had to be developed. It was decided to built this special type of burner as the biogas project at this stage had reached a point where a full scale application looked to be imminent. The fuel/burner system designed and developed by the author differs substantially from the classical design in that it resembles a common rail system rather than a single point injection system. A prerogative was further to use only air mixer burners with a high lambda value, using preheated air as combustion air, and hence a high flame exit speed for good flame depth

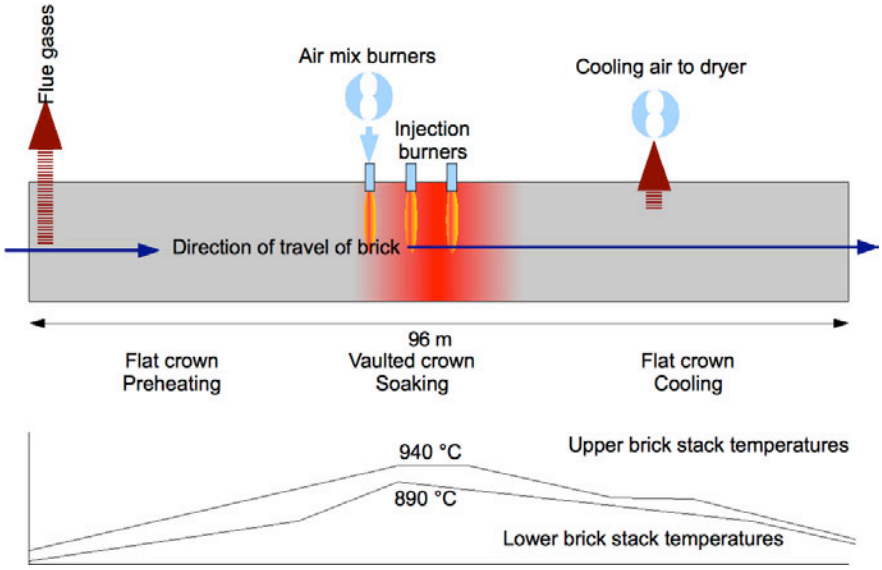
The modifications to the Ziegel Gasser Mattoni GmbH S.r.l. kiln and the dryer took place over a two year period during 2003 and 2004. It was necessary to modify the kiln and dryer to better utilise the technical requirements of the new feedstock containing a higher percentage of body fuel and the alternative fuels.

The starting situation for the kiln modifications is pictured in Figure 48. The firing curve is drawn based on data collected with Seger cones, a very rudimentary method as some of them had to be placed or removed through the stokeholes in the roof of the kiln with a purpose built caliper. This method however allows to obtain temperature data with no investment and low cost basic data.

The 1964 built tunnel kiln had been heavily modified in 1980 when both the pre-heating and the cooling zone were rebuilt. The original vaulted design was abandoned and a flat-roof with external thermal isolation chosen for the pre-heating zone and a suspended ceiling solution for the cooling zone.

At the same time an automatic setting machine for stacking the bricks on the kiln cars had been installed. The technology available at that time did not allow for an automated tapered setting.

Fig. 48: Ziegel Gasser Mattoni GmbH S.r.l. tunnel kiln (not to scale)



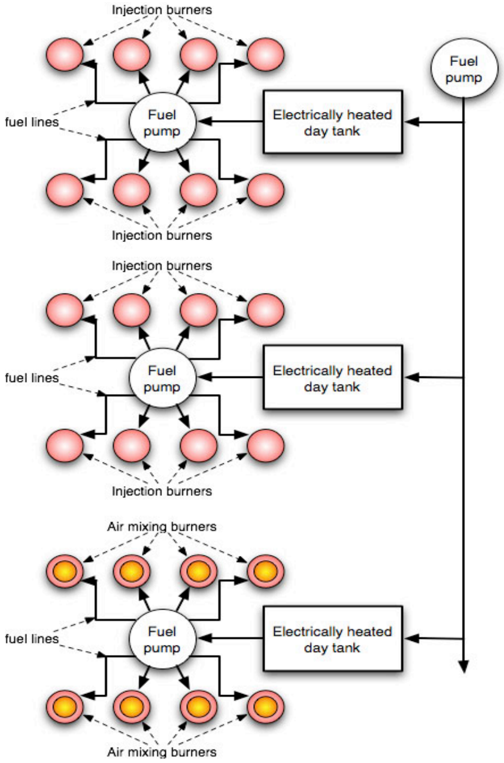
A kiln can be roughly divided (see page (35) for more details on the firing cycle into three major zones: the preheating zone up to about 650°C, the firing or soaking zone in which the desired firing temperatures are reached and kept for a given time to achieve the desired reactions, and the cooling zone in which the bricks are cooled down to a temperature that allows handling. The modifications to the pre-heatiing and firing zone lowered the overall useable height of the kiln. The modified ceilings rest on the side walls. This no longer allows use of the full 2 meter height of the kiln by stacking the bricks in a tapered shape on the kiln cars. The reduced stacking height left, a substantial gap in the vaulted firing zone between the maximum height of the arched roof and the upper layer of the now only 1.75 m height stacked bricks. Through this gap, the hot gases in the firing area can flow away very quickly and with almost no resistance. This particular design, however, makes it difficult to obtain very low energy consumption.

A relatively high temperature in the roof was further required in order to achieve, at minimum, acceptable temperatures at the kiln car level to achieve some kind of ceramic transformation.

The burner system, installed after the modification, consisted of 3 sets of 8 burners each: Two sets of injection burners and one set of air mixing burners. In this system each single burners had its own fuel line from the central injection pump connected. This burner system did also have an insufficient firing capacity. On average each of the injection burners had a firing power of 90 kw and the air mixing burners one of 100 kw. The total firing power installed on the kiln was hence just over 2 MW or 7,488,000 kJ. The average production is about 60 tons per day. The installed burner system required about 4 hours of maintenance per day due to lack of adequate filters and pumps. Usually fuel temperatures, for a #6 boiler oil as the one used by Ziegel Gasser Mattoni GmbH S.r.l., must be around 110 °C to 115 °C in order to achieve good combustion. At Ziegel Gasser

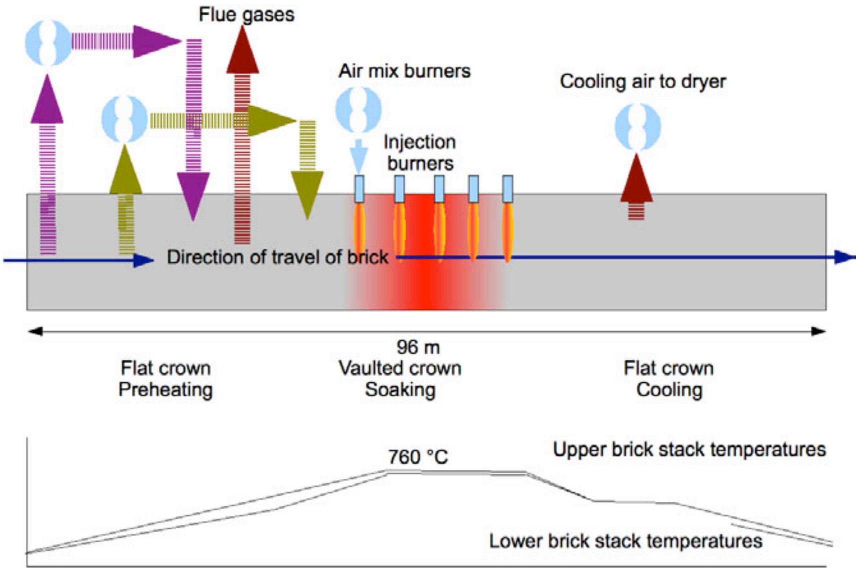
Mattoni GmbH S.r.l. due to poor isolation of the fuel lines and insufficient heating in the day tanks this temperature was found to have to be around 70°C to 80°C.

Fig. 49: Firing system prior to modification



The direction of travel of the brick in the above diagram would be from the bottom to the top of the drawing. The Ziegel Gasser Mattoni GmbH S.r.l. kiln did have in origin installed two lateral flue gas recirculation channels in the preheating section. These had been closed in the course of refitting the kiln with boiler oil burners for no apparent reason. In occasion of the winter 2001/2002 maintenance stop the closed channels were opened again, cleaned and new ventilators of greater capacity, about 20,000 Nm^3/h, installed.

Fig. 50: Ziegel Gasser Mattoni GmbH S.r.l. tunnel kiln after conversion



The installed fire power was increased by 16 burners each of a firepower of 90 kWh resulting in an additional firepower of 1.44 MW bringing the total firepower to 3,5 MW. This did not result in an increase in the average production but the outcome was rather that it was possible to lower the firing temperatures due to better heat distribution within the kiln and expose the bricks for a longer period of time to soaking temperatures. Peak production was doubled from 60 tons/day up to a maximum of 120 tons/day for certain very light and thin walled formats of brick.

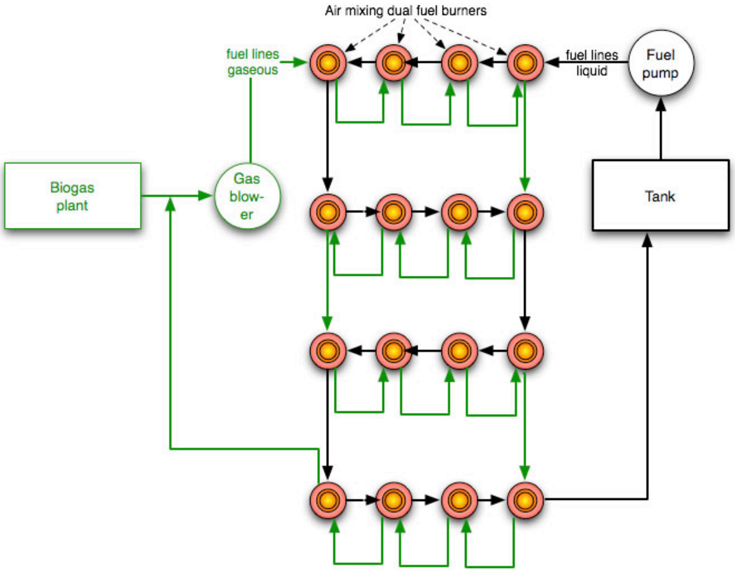
The advantage of having existing recirculation channels in the brick side walls of the kiln was, that no drop in temperature occurred due to the side channels surface having the same temperature as the kiln. The original system was modified into a two stage system in order to achieve higher rates of recirculation in the pre-heating zone of the kiln at the beginning of which low temperature carbonization gases are released from the organics contained in the brick body that contribute to lower brick density. In a traditional tunnel kiln these gases are expelled, without any energetic gain, through the chimney. They are a source for substantial air pollution if no external post-combustion system is installed. The flue gas extraction point of the Ziegel Gasser Mattoni GmbH S.r.l. kiln was moved from the beginning, entry of unfired product, of the kiln towards a position in proximity of the first set of burners. The Ziegel Gasser Mattoni GmbH S.r.l. kiln continued to be a full counter current kiln as the recycling fans kept a sufficient backdraft to have hot gases flow towards the beginning of the kiln.

In the preheating zone a very high rate of turbulence was achieved contributing sensibly to an uniform heat distribution across the horizontal and vertical section of the brick stacked on the kiln car. This resulted in a more uniform temperature distribution and hence lesser difference in compressive strength from the top to the bottom of the kiln. It also offered the chance of lowering firing overall firing temperatures. It was not more necessary to over-fire the bricks in the roof in order to achieve a sufficient ceramic transformation process for the lower layers. Moving the point of extraction of the flue gases forward did have a negative influence on the overall thermal energy balance, greater energy loss due to a maximum of 225°C higher flue gas temperature. This loss was however compensated for by a higher yield of the dryer to which a part flow of the hot flues gases are conveyed.

The combustion air in the Ziegel Gasser Mattoni GmbH S.r.l. system is preheated and taken from the forced cooling zone of the brick kiln at a temperature of about 200 °C. This results in fuel savings of about 10 %. Junge in his papers (302) (303) assumes savings of about 15 to 20% in cases where preheated combustion air is used. The savings indicated by Junge have not been observed in this work. The hotter combustion air allows a larger volume of air to be injected into the kiln, creating turbulence and hence, by better mixing, a more uniform temperature distribution across the kiln in both cross and longitudinal section. The larger volume of air, however, does not change the mass balance of the kiln.

In order to be able to fire a liquid and a gaseous fuel, especially one of potentially low quality and low to medium calorific value such as biogas, a special type of burner was requested. Burners, specialist equipment specifically designed, as the ones required have not been available on the market (and are not yet available).The liquid fuel part of the system developed is based on a constant fuel flow to the burners, each fitted with a computer controlled magnetic valve dosing exactly the quantity of either fuel required to maintain the kiln temperature level required. A central pump, backed up by a spare with an automatic switch over system, delivers a fuel flow of approximately 8 to 11 times the maximum consumption per hour of the entire system. The pumps are of the positive displacement type, piping is of mild steel with teflon gaskets and the burners are of stainless steel with critical parts in ceramics and titanium. None of this technology is available from the shelf. The temperature of the rendering and recycled frying fats and vegetable oils is kept at around 75°C to 85°C.

Fig. 51: Ziegel Gasser Mattoni GmbH S.r.l. dual fuel kiln burner system
(Safety and pressure valving is not pictured in the above sketch)



The gas feed line is built in a fashion similar to the liquid fuel line. A pressure valve on the return line assures a constant pressure at each burner. Excess gas is released into the pressure-less biogas storage tank but put into recirculation. All control systems are computerized and the gas systems for safety reasons redundant.

The detrimental affect of tallow on the burners necessitated careful cross-engineering and the adoption of materials and machinery in use by the food sector. No guidance was available from the industry, due to the unique nature of the candidate’s applied research program. As designed it can use either gaseous or liquid fuels, or a combination of both fuels at the same time.

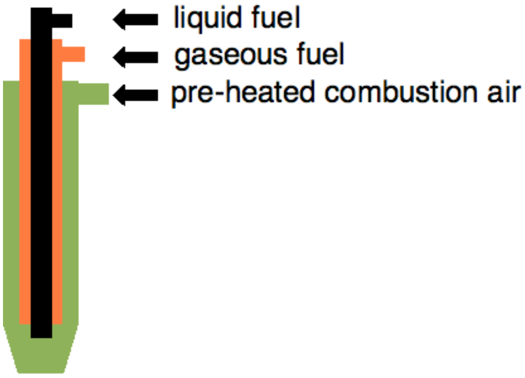
Dual fuels systems have not yet become state of the art.

A firing capacity of at least 90 kw for each position was required. The burners are made up of a series of concentric pipes of different diameter: The outer pipe is used to convey combustion air, the second to convey gas and the center one to convey the liquid fuel. The gas pipe is used to cool the liquid fuel pipe to temperatures below 100°C in order to avoid the formation of deposits at the tip.

The fuel flow for each burner can either be regulated such that one or the other fuel is burning continuously, one is burning continuously but the other intermittently or both are burning intermittently.

A special designed burner head allows for mixing the different fuels keeping a steady outer flow of air that helps shape the flame avoiding a “bubble” shape that would damage the brick on firing because of the flame getting in contact with the brick surface.

Fig. 52: Ziegel Gasser Mattoni GmbH S.r.l. duel fuel kiln burners

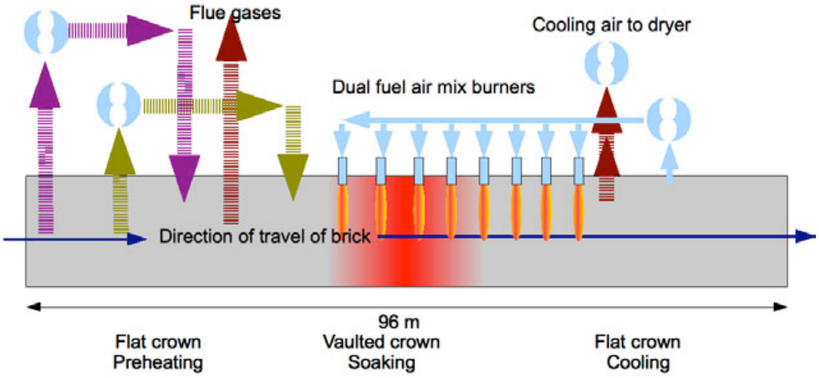


The above sketch is not to scale. The burners work on the pilot flame principle: If no gas flame is observed then liquid fuel is injected until a flame can be observed. This guarantees combustion of the biogas even if methane concentrations should be insufficient for an autonomous combustion. In the design particular care has to be taken to ensure that the pre-heated combustion air does have a volume and flow speed not exceeding about 1.5 times the flow and air speed of the gas in order to avoid dilution of the gas beyond ignition concentration. The speed at which the combustible mix leaves the burner is, depending on the fuel mix, 100 to 150 m/s.

The total investment for the new burner system at Ziegel Gasser Mattoni GmbH S.r.l. amounted to 135,000 Euro.

The overall modifications of the kiln and dryer system had made out of the original tunnel kiln at the beginning of the research and development work and a sophisticated firing apparatus has been created:

Fig. 53: Ziegel Gasser Mattoni GmbH S.r.l. modified tunnel kiln



The thermal balance for the Ziegel Gasser Mattoni GmbH S.r.l. kiln/dryer system before (2000) and after modification (2005) made based on the research by the author has been calculated to be:

Table 73: Effects of kiln modifications and alterations on specific fuel consumption and emissions

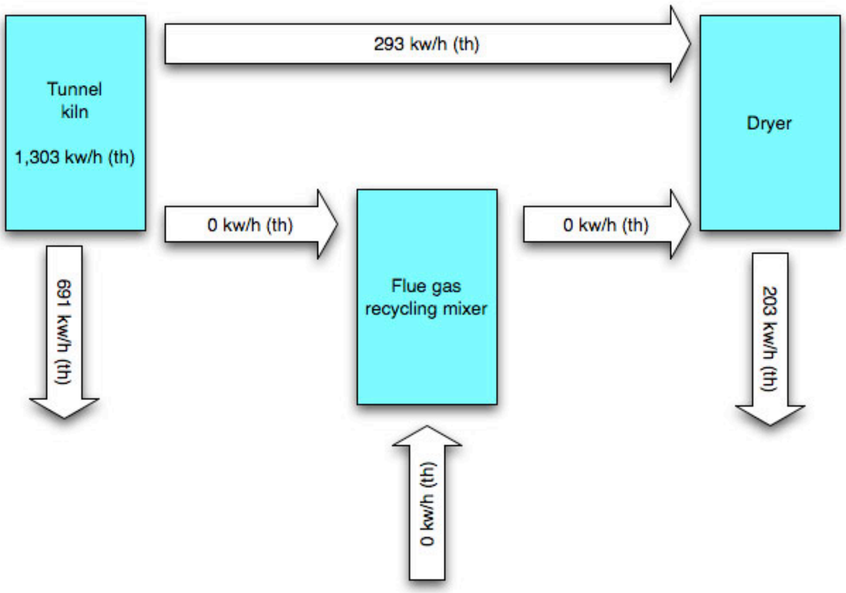
		2000	2005
Production	t/y	19,771	19,053
Hours of operation of plant	h/y	8,160	8,160
Peak production	t/day	80	120
Average production	t/day	60	60
Specific fuel consumption	kJ/kg	2,326.18	1,749.46
Body fuel (sludges and ashes)	kJ/kg	0	982.13
Total energy to kiln	kJ/kg	2,326.18	2,731.59
Flue gas loss	kWh	691.33	533.75
Flue gas temperature	°C	85	175
Flue gas volume	Nm3	40,000	15,000
Rapid cooling	kWh	293.57	273.99
Cooling air temperature	°C	75	105
Cooling air volume	Nm3	15,000	10,000
Flue gas heat recovery	kWh		889.85
Flue gas heat recovery temperature	°C		175
Flue gas heat recovery air volume	Nm3		25,000
Air mixer flue gas heat recovery /ambient air	kWh		1,148.48
Air mixer flue gas heat recovery /ambient air temperature	°C		110
Air mixer flue gas heat recovery /ambient air volume	Nm3		40,000.00

The pre-existing system might be considered to be more efficient from the point of thermal losses into the atmosphere. But it must be kept in mind that the primary energy used, i.e. the quantity of energy paid for, in the modified system is much less albeit the overall energy balance is resulting in higher energy consumption.

The above energy consumption and use diagram does only takes into account net amounts of energy and not energy introduced into the system by combustion of low temperature carbonization gases from the flue gas recirculation system or energy gains obtained using preheated combustion air.

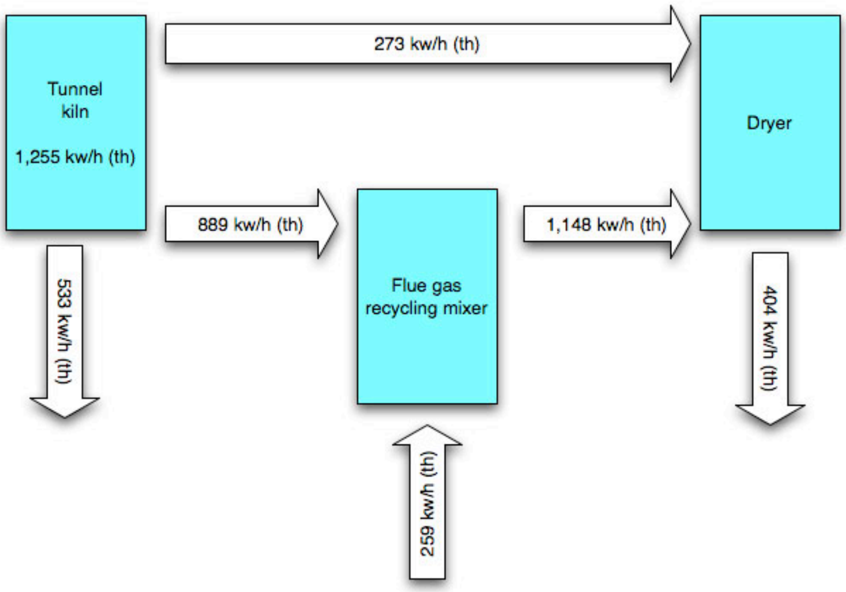
Figures 54 and 55 below describe the effects of the modifications on the energy flows in the brickyard:

Fig. 54: Kiln / dryer assembly before modification



The figure above illustrates the energy flow prior to the modification and the figure below the energy flow after the modification.

Fig. 55: Kiln / dryer assembly after the year 2004 modification



In Table 74 the fuels used, the specific energy requirement and emissions are listed.

Table 74: Effects of kiln modifications and alterations on specific fuel consumption and emissions in mg/Nm3 at 18% O if not otherwise indicated.

	2000	2001	2002	2003	2004	2005	2006
Firing temperature °C	940	940	760	820	820	860	860
	#6 boiler oil		#6 boiler oil rendering fat		rendering fat		rendering fat frying oil
				Flue gas recycling system			
					Purpose built burners		

	2000	2001	2002	2003	2004	2005	2006
Firing temperature °C	940	940	760	820	820	860	860
						Higher firing temperatures for better mechanical strength	
kJ/kg brick	2,326.18	2,156.65	1,752.66	1,686.06	1,446.52	17,49.46	1,936.22
Dust	48.00		5.00		2.63	< 0.05	2.63
NO_x as NO_2			n.a.		22.0	< 1	< 1
SO_x as SO_2	24.00		200.00		4.53	8	8
Fluoride as HF	7.70		20.00		0.28	< 0.02	< 0.05
Chloride as HCl	32.30		50.00		4.04	< 0.05	< 0.02
TOC			n.d		Not measurable		
Ethanol average					< 0.1		
Benzol					< 0.1		
Methanol average					< 0.1		
Phenol					< 0.1		
Formaldehyde					< 0.1		
Aldehyde (S C1 – C4)					< 0.1		
Carbon monoxide					78.52	< 1	8
Toxic equivalent I-TEF ng I-TEQ/m^3			0.1		0.004 -> < 0.0005		

These values compare favourably to the European industry BREF/BAT data (see: Appendix IV /page 174) results . Only the total sulfur emission is slightly higher than the lowest emission value of the European industry. All other values are well below the minimum values indicated in the BREF/BAT document. The Ziegel Gasser Mattoni GmbH S.r.l. firing system and utilization of an alternative fuel is well exceeding the state of the art of the industry. The very low contamination values of the flue gases, especially for fluoride and chloride, allow the flue gases to be recycled directly into the dryer adding a substantial quantity of energy for drying bricks. Considering that usually only cooling air from the rapid cooling zone of the kiln is conveyed to the dryer, this allows for a far higher volume flow of air in the dryer resulting in greater turbulence and hence more uniform drying of the single bricks.

The effect of adding rendering fat to the fuel itself in a kiln fitted with an internal post combustion system like the one developed at Ziegel Gasser Mattoni GmbH S.r.l. is interesting: A drastic reduction of the pollutants emitted can be observed.

5.3 Conclusions

Except for Ziegel Gasser Mattoni GmbH S.r.l. here are a few single examples (if one does not consider small scale rural brick making in industrializing or developing countries) of use of substitutive forms of energy. Sawdust is used in France by Imerys, olive and peach stones by SBBC in Morocco (but use is limited to the dryers) and landfill gas and synthgas from wood and carpeting manufacture byproducts is used by Boral Bricks in the US in three different plants. A few examples of plants running on landfill gas exist in Germany, Spain and the UK. Vegetable oils are currently not used by any. Recycled oils have been used by a plant in Germany and one in Austria but both applications have been halted.

Any form of substitutive energy requires additional efforts and utilization of non standard machinery and techniques. Any change in the cost of energy does not create a market distortion as the change is common to all actors.

All sources of energy used in a brickyard must match the production cycles, periods of operation and extended production stops, of the plant itself. Authorization for the use of the particular source of energy must be obtained. Unfortunately there are no guidelines for the use of substitutive sources of energy in a brick yard and this makes the authorization procedure complicated and difficult: the authorization body does not have any reference upon which base its decision.

A biogas plant, for example, cannot be stopped and restarted according to the utilization cycles of the brick plant. Generating electric energy outside the production cycle of the brick yard requires additional investments. A solution would be to feed the biomethane, once it has been purified, into the distribution grid. In some countries, like for example Germany, such a possibility has now been created by the legislative bodies. The cost of purification of the biogas in order to obtain biomethane varies, depending on fermenter technology and substrate, between 1 and 3 Eurocent per kw or about 8 to 25 cent per Nm^3 of biomethane. At 8 Eurocent per Nm^3 the project might be financially viable, at 25 certainly not. The digestate can be stocked and used as an addition to the brick feed. Biogas is a really viable alternative if for the substrate used gate fees can be obtained. In this case even very high treatment costs can be offset. At this point biogas is no longer an auxiliary activity to brick making but might well become predominant although no off-the-shelf solutions are currently available.

The use of landfill gas is not, unless as a source it is conveniently located, any easier. The treatment cost of landfill gas in order to bring it up to a quality that can be fed into the grid is certainly higher than for biogas.

Synthgas, either from raw materials or from waste streams, could be a viable alternative. Generation technologies are available and these might work if the gas is not to be fed to an engine or turbine but used as fuel in a tunnel kiln. A synthgas generator can be turned off and on as needed. Synthgas and landfill gas might be best used, due the very low calorific values, in a mixture with other fuels.

For this gaseous substitutive fuels no off-the-shelf burner technology is available today. Some technology might be adapted and used.

For solid substitutive fuels, no burner technology, not even in the aforementioned small artisanal plants, exists on the market. Hence this technology would have to be developed from first principles. For finely ground solid fuels, similar technology to that used for coal firing power plants might be usefully adapted and adopted. An alternative might be to use combustion chambers outside the kiln and convey only the hot gases.

Used and vegetable oils make an excellent fuel, especially if used in co-combustion with a gaseous fuel. No technical barrier exists for the use of such fuels.

Chapter 6

A South Tyrolean Case Study: Mattoni Gasser Ziegel GmbH S.r.l.

Advances in the utilization of waste materials and energy sources in brick making

Biogas

6.1 Biogas

This research and development project has received public funding from the renewable energies program of the Autonomous Province Bolzano[1].

Since the early use in 1895 as fuel for street lamps in the town of Exeter in the UK, biogas has come a long way [(304) Deublein and Steinhauser pages 27 to 43] . The state of the art of biogas generation today is almost exclusively represented by single or two stage fermentation systems sometimes integrated with a large capacity post digester.

The advantage of biogas is, that it can be used without restrictions for the entire kiln.

In order to recover energy from biomass a number of processes can be applied that depend on the C/N ratio and humidity content.

- Thermochemical conversion processes such as direct combustion, pyrolysis or gasification are most suitable for cellulose and wood rich wastes featuring a C/N ration greater than 30 and a humidity content inferior to 30. Most appropriate for a thermochemical conversion process is hence wood, it's by-products and lignocellulosic products such as grass, straw and some production wastes such as shells, nuts, and similar.
- Biomasses with a C/N ratio inferior to 30 and featuring a dry matter percentage inferior to 30, like for example leaves, stems, etc. present themselves to be used in a biochemical conversion process , anaerobic digestion, a biochemical conversion process in a reducing, oxygen poor, environment, causes the breakdown by micro organism of complex organic substances such as lipids, proteins and glucosides that are contained in both vegetal and animal biomass. It is a biological stabilization process aiming to reduce the C/N ratio by ways of digestion of the organic matter that allows the production of energy.

The generation of biogas from biomass within a brickyard can provide for a considerable reduction of fossil fuel consumption. The research and development work co-ordinated and overseen resulted in an international patent for a novel biogas generation technology. Careful analysis soon demonstrated the potential problems associated with a single-stage fermentation system. A paper by Kim et al. (305) indicates the advantages of a multi-stage fermentation system. The separation of the single phases of the process, hydrolysis, acidification and methane metabolization in different treatment vessels and reactors, allows an easier control of the pH values and reduces the risk of over-acidification by formation of free acids. Over-acidification leads to much longer times of residence of the biomass in the fermenters and hence to larger and more difficult to control plants.

A further advantage of the generation of biogas from biomass within a brick yard results in the total usability of the fermentation waste thereby avoiding the need to spread these wastes on farmland as fertilizer. Hence, for Ziegel Gasser Mattoni GmbH S.r.l., it was important to assess, within this aspect of the project, the possible utilization of the fermentation wastes in brick making. The addition test had to be made with concentrations that would exceed the later expected mass flow that would have had to be used if a full size biogas plant would be built. This resulted in a calculated addition of about 3% dry matter fermentation wastes to the brick feed. The fermentation wastes in the concentration re-

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[1] Massnahmen zur Förderung der Forschung und Entwicklung LG vom 13.2.1997, Nr. 4 Autonome Provinz Bozen Südtirol

quired can be used as brick body density reducing agent agent for low density bricks without any negative influences on quality or chemical composition of the green or fired bricks. On the contrary, it appears from the tests that the organic sludge tends to increase plasticity of the feedstock as visible from the Pfefferkorn tests carried out when used on a trial base and by the slightly reduced energy consumption of the extruder.

For the first fermentation tests in 2002 a small specially built trial plant was used.

Fig. 56: View of the first pilot biogas plant

Fig. 57: Function diagram of the first pilot biogas plant

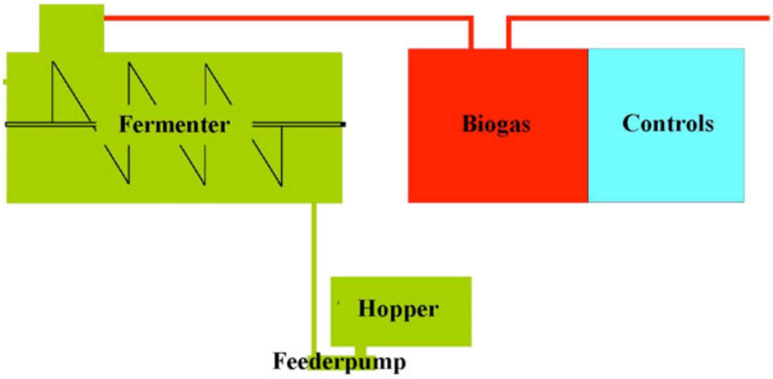


Table 75: Main technical specs of first pilot biogas plant

Feeding	Hopper 2 m^3 Propeller mixer 1,5 kW, 900 rpm
Fermenter	Volume 48 m^3 Horizontal mixer 3 kW with central heated axle All necessary fittings and couplings
Electrics & Electronics	Substrate feed meter Gas meter Automatic gas analyzer Thermocouples fermenter

Various sources of biomass have been laboratory and / or pilot plant tested in order to evaluate quality and yield of biogas by mesophilic fermentation.

Table 76: Gas yield of various organic substances tested in either of the biogas plant's built and operated.

Type of biomass	Biogas in l/kg dry matter
Kitchen wastes	0,7–1,3
Biodegradable packaging	0,64

Type of biomass	Biogas in l/kg dry matter
Packaged food production wastes	0,32–0,8
Slaughterhouse wastes	0,34–0,71
Organic based oils and greases including lubricant oils	> 0,5
Fishing wastes	≙ 0,5
Differentiated waste collection	0,40–0,58
Potato wastes	≙ 0,48
Wastes from the production of drugs	0,2–0,75
Potato distillation residues	≙ 0,46
Beer production residues	0,42–0,5
Fruit distillation residues	0,45
Green waste	0,35–0,46
Sewage sludge	0,39–0,41
Manure	0,22–0,55
Paper and cardboard production wastes	0,2–0,3

Whereas the chemical composition of the biogas is:

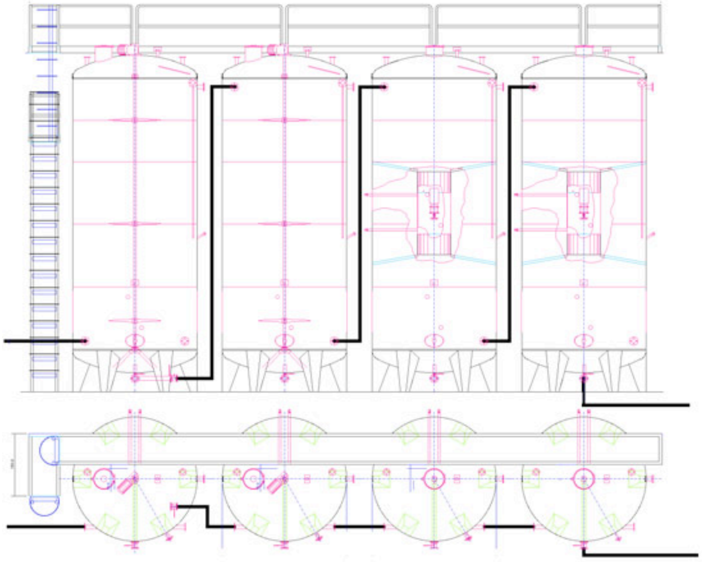
Table 77: Chemical composition of the biogas in % if not otherwise indicated

Methane	40-75
CO_2	25-55
Water vapor	0-10
Nitrogen	0-5
Oxygen	0-2
Hydrogen	0-1
Ammonia	0-1
Hydrogen sulphide	0-1
Density	1,2 kg/Nm^3
Lower calorific value	3 400 – 6 400 kcal /Nm^3
Ignition temperature	650 – 750 °C
Ignition concentration	6 – 12 % vol
Liter equivalent fuel oil Nm^3 biogas	0.60 - 056
Smell	depends on substrate

The above data were obtained from trial runs using either of the plants built at Ziegel Gasser Mattoni GmbH S.r.l. or with tests using a laboratory fermenter at the Fachhochschule Trier.

After termination of the trial runs with the sea container size plant it was decided to move one step further and built a pilot plant based upon the experience gained with the small installation. The Ziegel Gasser Mattoni GmbH S.r.l. technology is based on a cascade of single fermenters and separate acidification and hydrolization stage. The plant, when compared to traditional biogas plants, is of much smaller size and eliminates the need, due to the patented cascade fermentation, the need to dispose of waste waters having a high organic content, i.e. the effluent can be fed either to the main sewer or used in other processes.The plant described in Fig. 58 was designed and built.

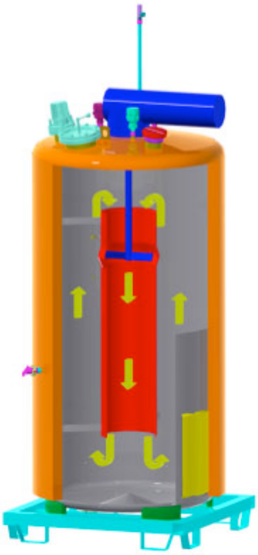
Fig. 58: Drawing of the second pilot biogas plant



The cascade fermentation system consists of a series of stainless steel vessels in which the substrate flows semi-continuously from one vessel to the other (initial feed → hydrolysis → acidification → multi-step methane generation).

To achieve a better agitation of the substrate, the vessels are flow optimized and fitted with continuous loop mixers.

Fig. 59: Continuous loop mixer fitted in fermenter



Process conditions (temperature, pH value, retention time, mixing) of each vessel can be varied according to substrate requirements and operational data. The relatively small size of the single vessels allows for relatively rapid changes of the most important process parameters favoring substantial efficiency improvements.

The anaerobic cascade biogas digestion process allows for a wider choice of substrates and mono-substrates such as, for example, fruit marc and organic waste. Given the highly efficient temperature-controllable hydrolysis, a plant such as this can easily be adapted to work with very difficult substrates that, in other biogas plants, could either rapidly degrade the fermentation process or be used only as co-substrate.

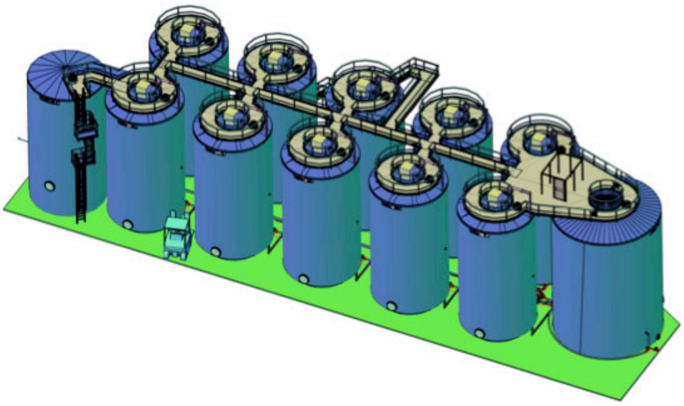
The main differences between the novel cascade fermentation process and the state of the art are illustrated in Table 78. The higher investment required for a cascade fermentation system certainly targets the possible application to installations where somewhat more stringent requirements exist - like for example in the case of organic household waste as monosubstrate. In this case the higher investment and greater complexity is offset by the higher commercial yield of the plant. Another possible advantage of the cascade fermentation system is a higher operational safety and process reliability compared to a traditional plant because of the separation of the phases and the single, relatively modest sized, vessels. An advantage of this design is that the entire plant is not necessarily affected contamination of incoming feedstock but only a limited portion of the overall digestion volume.

Table 78: Comparison of anaerobic fermentation systems

	Single stage fermentation	Two stage fermentation	Cascade fermentation
Characteristics	Biochemical processes take place in the same vessel and partially in competition between each other. Poor mixing and poor phase separation. Biogas contains between 35 and 60% of methane. Up to 20% of dry matter and hence very high COD values in the effluent.	Rough separation of the biochemical process phases. Improved yield and most of the times biogas featuring a higher methane content. Improved mixing but still insufficient phase separation. Lesser COD and dry matter content in the effluent.	Complete separation of the biochemical process phases improving further on methane content in biogas. Individual temperature control of the various stages and phases. Very low COD and dry matter content in the effluent. Very efficient mixing and good phase separation.
Investment	Low investment.	Medium investment.	Higher investment.
Suitability	Best suited to plants in an agricultural environment where the effluent is to be used as fertilizer and the main objective is manure odor treatment.	Mostly used for energy crops.	Accepts wider choice of substrates. Works well with monosubstrates.

The continuous cascade biogas digestion process (Figure 60) is based upon the spatial separation of different phases of the biological process into well-defined spaces that allow, when compared to traditional fermentation systems, for a specialization of the various stems of archaea . This results, under controlled and analyzed conditions, in higher biogas yield and better digestion.

Fig. 60: Artistic rendering of biogas plant



Furthermore, the spatial separation allows for complete control of the bacterial activity as the transfer flow between the single vessels can be sampled, analyzed and, depending upon the result, any necessary corrective steps taken. The single vessels do not need to be of the same size but can be of different size in order to best accommodate the duration of each specific process stage. Bypass feeding, i.e. not utilizing the entire cascade for some given substrates, is also possible, adding further to the flexibility of the plant.

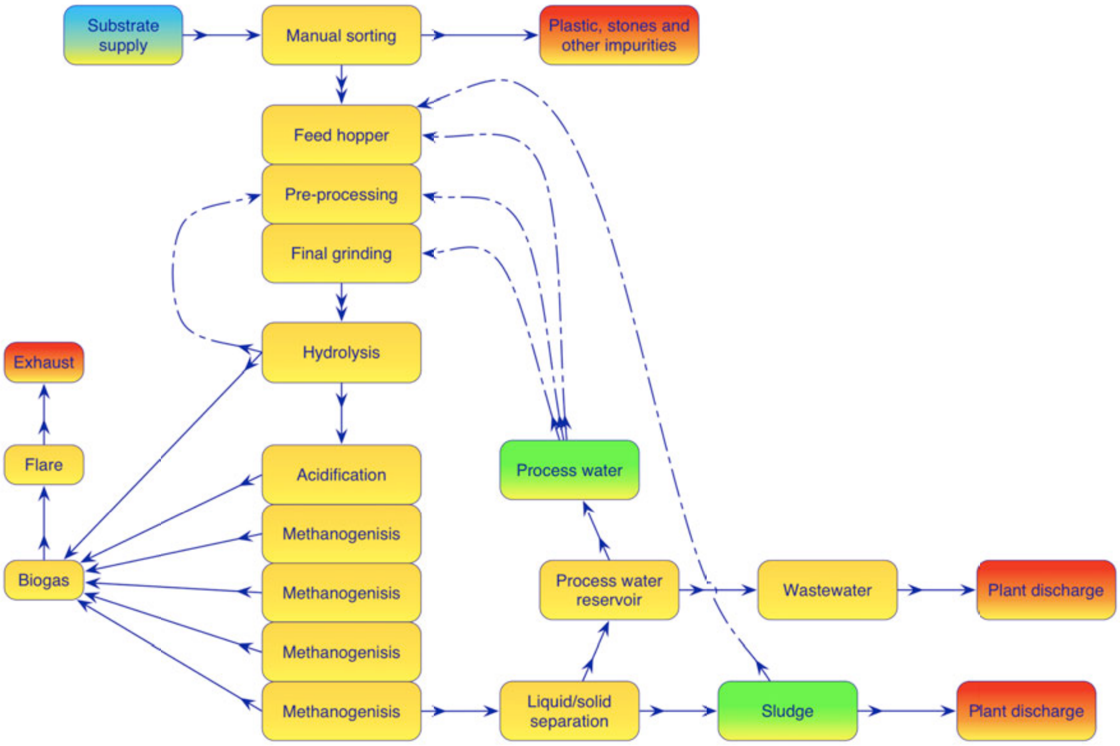
The substrate is, prior to being fed to the system, ground or crushed to a particle size of less than 5 mm. It is then fed, after having been heat treated for hygiene, to the hydrolysis vessel. The loading level of this temperature-controlled vessel can change according to process needs.

The feed to the subsequent acidification vessel can either be continuous, semi-continuous or batch. From the acidification vessel the substrate is fed in continuous to the first of the methane generators.

In the first stage of the methane generating process, organic matter is decomposed by mainly acetogenic strains of bacteria at a pH value between 6.5 and 7. The pH value in this first stage is controlled accurately by the feed rate.

In the second stage methane generation occurs to a lesser extent by acetogenic and to a larger extent by hydrogenotrophic bacteria. In the subsequent stages the hydrogenotrophic archaea strains become more and more predominant and the pH values slowly rise to neutral or slightly above. Bacterial activity is controlled by temperature, any eventual addition ofenzymes, and temperature.

Fig. 61: Continuous cascade biogas digestion process



Installation of full size biogas plant would have resulted in very favorable economic conditions of operation for the brickyard if the plant would have been run on certain waste streams:

- 3.500 t/year household biowastes Autonomous Province Bozen South Tyrol, gate fee about 65 € per ton delivered;
- 1.500 t/year industrial biowastes IPRONA (production of fruit preserves), t/- 0 € per ton delivered;
- 1.000 t/year industrial biowastes PANA (production of apple strudel preserved cakes),), t/- 0 € per ton delivered;
- 5.000 t/year industrial biowastes VOG and Hans Zipperle AG S.p.A. (production of fruit preserves 15 € per ton delivered.

The cash flow of the biogas plant will hence be:

$$3{,}500\ \text{t/yr} \times 65\ \text{€/t} + 1{,}500\ \text{t/yr} \times 0\ \text{€/t} + 5{,}000\ \text{t/yr} \times -15\ \text{€/t}$$
$$=$$
$$152{,}500\ \text{€}$$

of revenues for the brickyard. Energy required to fire and dry the bricks would have been a source of revenues instead of a cost. Overall production costs, considering the use of wastes as well, would have been negative, i.e., the bricks could have been sold at any price greater than zero and the brick plant would still have remained profitable.

6.2 Biogas generation fermentation wastes

Disposal of the biogas fermentation wastes in agriculture as fertilizer was never considered an option. Hence new ways of disposal had to be investigated. The alternative of choice was using these wastes as a pore forming agent in brick making.

Tests using the fermentation wastes as an addition to the brick have been carried out. The tests have been made by adding a 10 to 12 % by volume of fermentation waste to the standard clay mix of the Ziegel Gasser Mattoni GmbH S.r.l. brickyard. Biogas is a very interesting source of energy for a brick yard but it poses the problem of disposal of the fermentation wastes. In most biogas plants the wastes are spread in agriculture as fertilizers. The Ziegel Gasser Mattoni GmbH S.r.l. brickyard, as most brick yards, is an important land owner but not a farming operation. The vast experience acquired with the utilization of sewage sludge encouraged to use the fermentation wastes on the same level with sewage sludges. For the purpose of testing, sludges expected to be of similar chemical composition to those resulting from a later full size plant at Ziegel Gasser Mattoni GmbH S.r.l. have been obtained from the "Vagron" biogas plant located in the Netherlands serving the Groningen region.

Production tests were run with 20% by volume of "Vagron" fermentation wastes:

Table 79: Comparative analysis brick / fermentation waste added brick

Impact category			Average 2000 /2001	Average 2002	Average 2005	Agreed threshold value	Vagron fermentation waste trial run
Oxides							
Aluminum oxide	Al_2O_3	mg/kg dry matter	15.61	13.96	13.6	< 25.00	13.70
Sulfur trioxide	SO_3		0.6	0.26	0.42	< 5.00	0.60
Antimony oxide	Sb_2O_3		1.02	1.2	2	< 5.00	< 1.20
Barium oxides	BaO		622.73	518	738	< 1,000. 00	550.00
Boron trioxide	B_2O_3		161.22	61	3180	< 500.00	150.00
Calcium Oxide	CaO		11.39	10.56	8.24	< 10.00	9.80
Iron oxide	Fe_2O_3		6.71	6.26	6	< 10.00	6.10
Phosphorus Pentox.	P_2O_5		0.38	0.28	0.64	< 0.50	0.42
Magnesium oxide	MgO		3.7	2.54	2.28	< 5.00	2.40
Manganous oxide	MnO		0.1	0.09	0.11	< 0.25	0.10
Lead oxide	PbO		147.42	65	45.8	< 150.00	73.00
Potassium oxide	K_2O		2.96	2.56	2.6	< 25.00	2.40
Silica	SiO_2		45.9	41.78	47.4	< 65.00	43.40
Sodium oxide	Na_2O		1.21	0.88	1.22	< 1.50	0.90
Titanium dioxide	TiO_2		8587.27	8700	8466.67	< 15,000.00	8,600.00
Zinc oxide	ZnO		293.45	163.4	163	< 1,000.00	240.00
Zirconium oxide	ZrO_2		318.27	275.8	300	< 450.00	290.00
Heavy metals							
Arsenic	As	mg/kg dry matter	23.84	19	16.6	< 50.00	16.00
Cadmium	Cd		0.82	1.5	<1	< 1.50	< 1.00
Σ Chromium	Cr		143.18	128.4	114.8	< 200.00	125.00
Mercury	Hg		1.23	1	<1	< 2.00	< 1.00
Nickel	Ni		77.27	73.8	67.4	< 100.00	71.00
Copper	Cu		45.09	36	37.2	< 500.00	47.00

Impact category				Average 2000 /2001	Average 2002	Average 2005	Agreed threshold value	Vagron fermentation waste trial run
	Selenium	Se	mg/kg dry matter	1.47	<2	<1	< 2.00	< 2.00
	Lead	Pb		n.d.	n.d.	n.d.	< 20.00	
	Zinc	Zn		n.d.	n.d.	n.d.	< 1.00	

The results clearly show that the use of organic household waste fermentation residues in the investigated quantities would not pose a problem as all values are well within regulatory and the Ziegel Gasser Mattoni GmbH S.r.l. benchmark limits.

Table 80: Comparative leaching values brick / fermentation waste added brick

Impact category			Production	20% Fermentation wastes average	Limit values (agricultural use)	Limit values (industrial use)
Fluoride	F	mg/l	1,5	1,1		
Chloride	Cl		13	3		
Nitrate	NO_3		<1	<1		
Sulphate	SO_4		155	93		
Arsenic	As	µg/l	7	6	20	50
Barium	Ba		6	4		
Beryllium	Be		<0,5	<0,5		
Cadmium	Cd		<0,5	<0,5	2	15
Cobalt	Co		<1	<1		
∢ Chromium	Cr		290	185	150	800
Mercury	Hg		<0,1	<0,1	1	5
Nickel	Ni		<1	<1	120	500
Lead	Pb		<1	<1		
Copper	Cu		<1	<1	120	600
Selenium	Se		<3	4	3	15
Vanadium	V		89	64		
Zinc	Zn		2	2		

The utilization of biogas organic fraction of household waste fermentation residues does not alter sensibly the chemical composition of the brick itself or its leaching behavior. It can be used in brick production as a density reducing agent without any major influences on the quality or chemical composition of the fired bricks.

The results of the above table have been obtained by adding a 20 % in volume of the solid fraction of the fermentation of organic household waste from the Vagron plant in Groeningen in The Netherlands to the standard feedstock of a brickyard.

As shown, the brick manufactured with the addition of the fermentation wastes will fulfill, at the end of its lifecycle, the requirements of current Italian regulation (152/2006) concerning recycling and reuse of building materials.

6.3 Conclusions

If the full size biogas plant would have been built, energy would have become a substantial source of income for the brickyard improving further the already good production cost standing (Fig. 62: Comparative production costs (net of overhead costs), page 146). The income would have been generated by the gate fees collected for the disposal of the organic wastes used as substrate in the plant.

The environmental impact would have been further substantially reduced (avoided methane emissions by organic waste either composted or landfilled).

Chapter 7

A South Tyrolean Case Study: Mattoni Gasser Ziegel GmbH S.r.l.

Advances in the utilization of waste materials and energy sources in brick making

Evaluation of results

7.1 Introduction

The results of this research and development work aimed at the reduction of the environmental footprint of the operation and return to profitability by both reducing costs and expanding clientele are deeply intertwined with each other.

Brick continues to be a low added value product. Targeting the environment conscious niche market like Ziegel Gasser Mattoni GmbH S.r.l. did certainly has paid. But has paid only at condition that the brick did not command higher, or at least sensibly higher, prices than the one offered by competitors. The “green” factor was a selling bonus. It is however a route that can be taken by a small manufacturer like Ziegel Gasser Mattoni GmbH S.r.l. but will certainly not be an alternative for the very large players in the market. These companies need to acknowledge the low intrinsic value of their products and lower their production costs considerably. Production costs, at current (2010) energy and raw material prices, can be estimated to be in the range of 20.—to 30.—euro per ton of product net of overhead, financial and distribution costs.

The modifications made to the production process give both tangible and intangible results.

The use of sewage sludge, fruit combustion ashes and fruit juice filtration wastes resulted in a reduction of the supply of quarried raw materials while the glass fiber cut-offs, used as a frit and to reduce drying shrinkage and cracks, resulted in a lesser quantity of quarried raw materials used and additional income from gate fees.

The use of the alternative raw materials contributed to the improvement of some product characteristics such as thermal conductivity (resulting in better thermal insulation of a building) but on the other hand required to install a kiln internal post-combustion flue gas recirculation system in order to cope with the low temperature carbonization gases emitted during the initial firing phase.

Using alternative combustibles lowered production costs and improved relations with external stakeholders due to lesser concentrations of contaminants in the emissions of the plant.

7.2 Results overview

The benefits and interactions, and hence advantages and drawbacks, of all the changes, improvements and modifications to the process can be best presented in the form of a matrix.

The tangible, measurable, benefits of the research work that generated current and fixed assets and had a direct effect on the cash flow of the company are given in Table 78:

Table 81: Modifications to the process – tangible benefits

	Sewage sludge	Fruit combustion ash	Fruit juice filtration waste	Glass fiber cut-offs	Rendering fat Frying oil	Biogas
Environmental impacts	Reduces consumption of quarried clay;	Reduces consumption of quarried clay;	Reduces consumption of quarried clay.	Reduced firing temperatures and hence re-	Reduced emissions.	Reduced emissions.

	Sewage sludge	Fruit combustion ash	Fruit juice filtration waste	Glass fiber cut-offs	Rendering fat Frying oil	Biogas
	Odor risk; Leaching into ground of stocked sludges.			duced emissions.		
Financial impacts	Additional income from gate fees	Transport cost.	Transport cost.	Lower firing temperatures hence lesser energy consumption.	Substantially reduced firing costs due to lower cost of fuel. Firing costs with waste vegetable oil comparable to firing with natural gas. Additional income from sale of energy efficiency certificates. Additional income from sale of CO_2 certificates.	Additional income from waste treatment (if certain wastes are used as substrate in the plant). Additional income from sale of energy efficiency certificates. Additional income from sale of CO_2 certificates.

Whereas the intangible, subjective benefits to the various stakeholders that can not be physically measured but that gave the company a competitive advantage over its competitors are indicated in Table 82:

Table 82: Modifications to the process – intangible benefits

	Sewage sludge	Fruit combustion ash	Fruit juice filtration waste	Glass fiber cut-offs	Rendering fat Frying oil	Biogas
External stakeholders benefits	Less quarry activities.				Cleaner emissions reduce impact on microclimate of operations.	Cleaner emissions reduce impact on microclimate of operations.
Internal stakeholders benefits					Reduced health risk due to fumes and contact with fuel.	

The positive change to the tangible and intangible assets of the company would have nevertheless impossible without the underlaying profound modifications to the production process and product:

Table 83: Modifications to the process – process and product

	Sewage sludge	Fruit combustion ash	Fruit juice filtration waste	Glass fiber cut-offs	Rendering fat Frying oil	Biogas
Process energy	Slight reduction	Slight reduction	Slight reduction	Sensible reduction.		
Product characteristics	Better thermal insulation qualities due to lesser density.	Better thermal insulation qualities due to lesser density	Better surface of product as alcohol contained in waste acts as a lubricant.	Slight, recurring surface defects due to craft paper and aluminum foil wastes mixed to the fibers.		
Feed	Requires a far higher accuracy in mixing and preparing	Requires a far higher accuracy in mixing and preparing	Requires a far higher accuracy in mixing and preparing			

	Sewage sludge	Fruit combustion ash	Fruit juice filtration waste	Glass fiber cut-offs	Rendering fat Frying oil	Biogas
	the feed.	the feed.	the feed.			
Drying	Increases humidity, more energy required for drying. Increases risk of drying cracks due to higher humidity	Reduces humidity of feed. Reduces risk of drying cracks.	Increases humidity, more energy required for drying.	Reduces risk of drying cracks.		
Firing	Firing curve needs to be adjusted to allow for higher organic content in the brick. Requires post combustion due to emission of low temperature carbonization gases.	Firing curve needs to be adjusted to allow for higher organic content in the brick. Requires post combustion du to emission of low temperature carbonization gases.	Firing curve needs to be adjusted to allow for higher organic content in the brick. Requires post combustion du to emission of low temperature carbonization gases.	Reduces firing temperature by about 75°C. Reduces risk of firing cracks.	Special burners, tank and fuel pumps required.	Special burners required.
Extrusion	Increases plasticity	Reduces plasticity.	Increases plasticity	Reduces plasticity. Needs frequent cleaning of the cutting wires. Automatic cleaning system installed.		

The overall result is, from an environmental and financial point of view, a positive one. The environmental impact of the product and the production process have, as documented by the EPD's, been reduced considerably and the financial situation improved greatly. The 2006 SWOT analysis, Table 49 on page 91, testifies to the success of the steps taken. Some research and development work, such as the biogas project, remained unfinished within the time frame of this thesis due to regulatory obstacles.

The intangible disadvantages are summarized in Table 81:

Table 84: Modifications to the process – intangible disadvantages

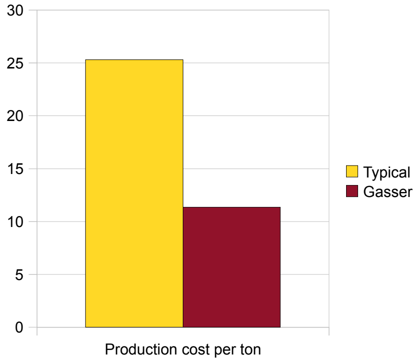
	Sewage sludge	Fruit combustion ash	Fruit juice filtration waste	Glass fiber cut-offs	Rendering fat Frying oil	Biogas
External stakeholders disadvantages	Odor. Transports.	Transports.	Odor. Transports.	Transports.	None	Odor
Internal stakeholders disadvantages	None.	None.	None.	Suspended fibers.	None	None

From the evidence collected and included, the use of wastes as an addition to or substation of quarried materials can be deemed safe and both environmentally and financially advantageous. Same can be said for the use of alternative fuels. In both cases certain precautions have to be taken.

The comparative study on breathable silica, see Appendix II, does not indicate that there are any health risks associated with the incorporation of waste materials into a brick body as long as some basic criteria, establishment of a site specific chemical composition standard, are strictly and methodically observed. This study is a first in the sense that in the examined or otherwise published bibliography such studies have never been made available to the public. It could well be that in other circumstances similar studies have been made, but certainly never comparing a waste amended and pure clay brick.

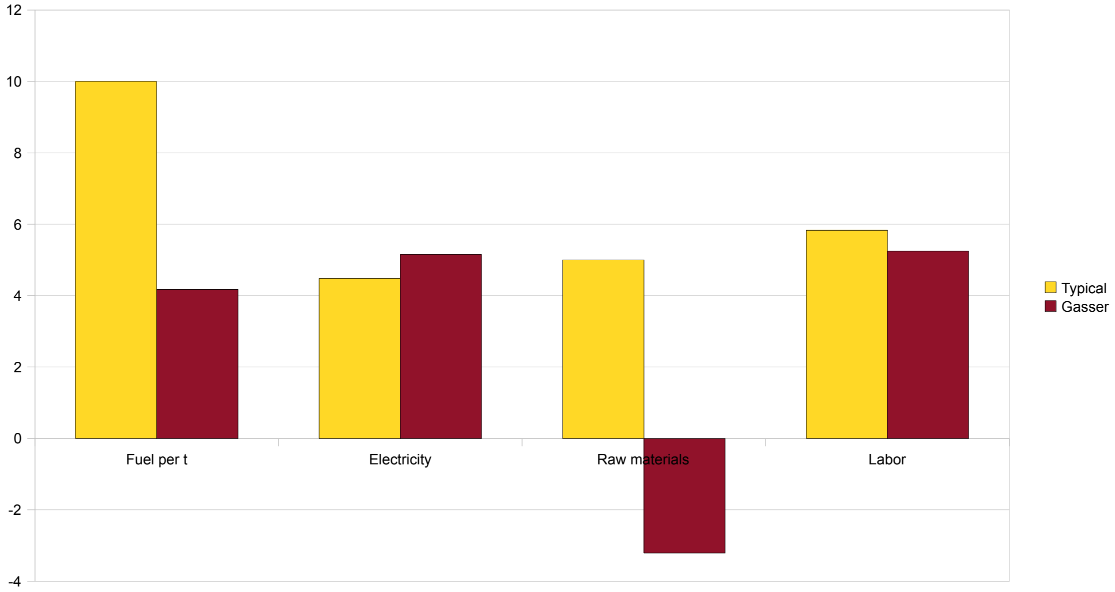
The production cost of Ziegel Gasser Mattoni GmbH S.r.l. and a typical Italian brick yard in €/ton net of overheads in comparison are:

Fig. 62: Comparative production costs (net of overhead costs)



Ziegel Gasser Mattoni GmbH S.r.l. is able to eventually turn a profit even under difficult marketing situations whereas other companies might start loosing substantially.The comparison between the impact situation prior and after the introduction of the alternative fuels shows a sensible reduction in the financial and environmental impact of the operation. Certainly if other alternative fuels would have been used, further modifications to the kiln, the burner and the flue gas system would have had to be made to cope with another type of fuel. It is however shown that such modifications can be successfully implemented and operated.Whereas the single expenses are:

Fig. 63: Itemized comparative production costs



The sum of all measure taken has hence had an overall positive effect on the operations of the brick yard and placed the the company in an enviable financial condition without causing or creating additional, not manageable, risks to the day-by-day operations or the product itself.

7.3 Lessons learned

In order to to achieve the results tabled a substantial change to the corporate culture was required. The work force had to accept leadership by a new person whose only apparent intent must have seemed to create trouble and break up well established norms, customs and habits. Recognizing that the new leadership was gearing primarily on assuring a future for the company came much later once the first tangible successes had been achieved. To make the way to success a little easier, job training courses, a motivation not to mutineer, have been organized on a regular schedule. In this way each of the workers had the possibility to trace back on his steps of pre-formed opinion without having to acknowledge failure (in thinking). Training did not only address the purely technical questions related to the production process but also stakeholder aspects such as environmental and market position. Notwithstanding this preemptive approach the situation was still characterized by the attitude of “the idea is good but we are not enthusiastic about it” and any momentum was lost quickly at the first difficulty.

Chapter 8

A South Tyrolean Case Study: Mattoni Gasser Ziegel GmbH S.r.l.

Advances in the utilization of waste materials and energy sources in brick making

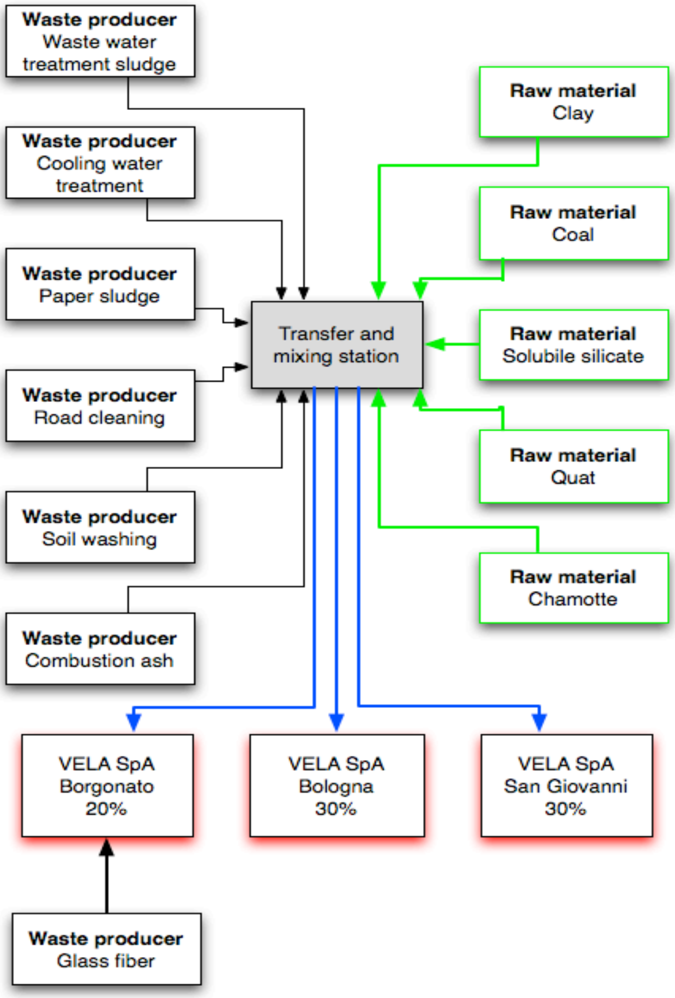
Continuation

8.1 Continuation - wastes

Based on the data collected over the years it is now possible to use a standard evaluation procedure that gives sufficient information about the possible risks of a full scale trial. The approach to full scale trials is also different: It is no longer envisaged to run a single trial and draw from this the information required but rather to run multiple trials in small increments will be used to establish the necessary data. This approach reduces the risks (also considering that the VELA plants on the average are 8 to 12 times in size of the Ziegel Gasser Mattoni GmbH S.r.l. plant).

The research and development work is continued at the moment mainly at Recuperi Industriali S.r.l. and, as far as use of premixed waste streams is concerned, at the Wienerberger and VELA plants in Italy. Some of the prior research and development work is applied on a minor scale at SBBC in Morocco. Some of the Wienerberger and all the major VELA plants today employ a waste based material feed. In the following Figure 64 the waste streams are given.

Fig. 64: Materials flow

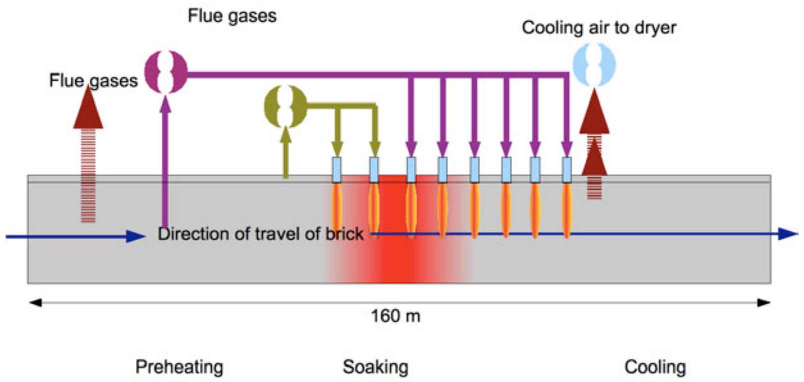


From the mixing process at the Recuperi Industriali S.r.l. transfer and mixing station a sophisticated feed with well accurately defined properties results. The complexity of managing waste flows makes the VELA approach of out-of-house mixing and preparation a logical choice. Furthermore it is not necessary to obtain waste permits for all production sites but only for one transfer and mixing station. The capacity of the Recuperi Industriali transfer and mixing station is about 250,000 metric tons per year. From the mixing station not a waste but a raw material is delivered.

8.2 Continuation - energy

The basic flue gas recycling concepts developed within this research and development work at Ziegel Gasser Mattoni GmbH S.r.l. is applied at the VELA Borgonato (and will be at the VELA San Giovanni) plant in a far more, as pictured below, sophisticated way:

Fig. 65: Working principle Borgonato kiln
(sketch – not to scale or indicating actual number of burners)



The longitudinal recirculation system draws the low temperature carbonization gases rich gas mixture from the preheating zone at a temperature in excess of 165°C and the maximum operational temperature of the existing burners of less than 185°C. The temperatures in the recirculation system are further dictated by the need to avoid condensation of long chain C-compounds within the system itself. The minimum oxygen content in the recirculation system is set to 6%. The acceptable temperature and draught balance left/right has been empirically set to 25%.

The injection burners in the soaking zone are fed with these gases and operated at a stoichiometric coefficient inferior to 1. Any not combusted matter in the kiln atmosphere is post-combusted once the gases are in contact with the flames of the micro pulsating burners located in the pre-heating zone.

The regulation of the stoichiometric coefficient is critical and needs to be carefully adjusted based on empirical data.

The sequential injection of recirculated gases results in the kiln operating not any more as a single chamber but rather as a number of sequential chambers consisting each of the brick stacked on the kiln car and the burner channel in front, in direction of travel, of each pack. In each burner channel the volume of gases injected back is such that pressure and flow conditions differ substantially from the preceding chamber. This causes very instable conditions of flow of the gases within the kiln with a very substantial positive effect on the heat transfer.

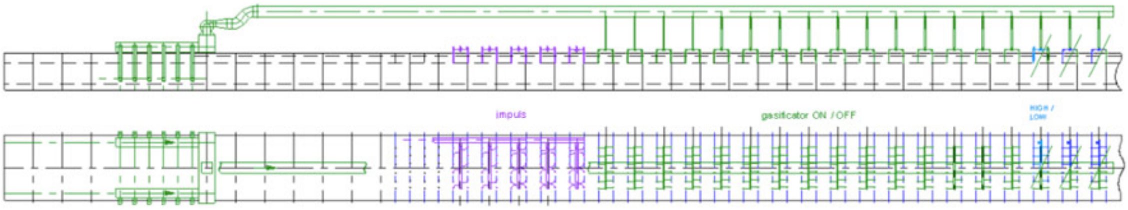
The recirculation results further in a reduction of emissions by post-combustion of the organic content of the low temperature carbonization gases.

A side effect is the easier management of the kiln in the case of greatly varying setting densities and a higher push rate due to a far higher volume of air recirculated in the kiln. It is now around 45,000 Nm3/h compared to about 6,000 Nm3/h previously. The total flue gas volume is about 75,000 Nm3/h, hence about 60% of the total volume flow are recirculated. This results in a flow in the soaking zone of about 120,000 Nm3/h resulting in much higher pressures within the kiln and much higher relative speeds fluid:solid and thus much better heat transfer rates. Injection pressure at the burners has been augmented from 200 mm to about 400 to 450 mm thus allowing for a longer, when the burner is actually working and not only used as an injector for the low temperature carbonization gases, and more poignant flame. The higher volume of air also makes for a lesser apparent flame temperature and hence reduces risk of flaming on the brick surfaces.

As a consequence of this recirculation, the free oxygen content in the soaking zone drops to values of between 4% and 8%. This reduction of the oxygen content in the soaking zone allows for a substantial reduction of the necessary firing temperature by reducing FeO from Fe_2O_3 (306)(307) and anticipating the release of efflorescence generating sulfate from the body.

The system drawn to scale:

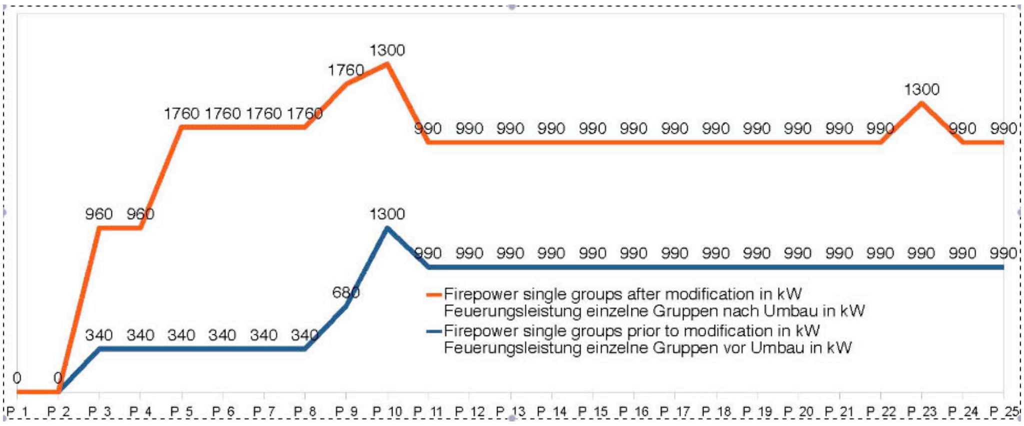
Fig. 66: Engineering drawing of the low temperature carbonization gases recirculation system



The burners in the preheating zone and just until the beginning of the firing zone, indicated in violet int he engineering drawing, are high power pulsating flame burners. Firepower is varied with the aid of an electronic controller in the milliseconds range in order to create a “pumping” air flow. These burners are fed with preheated, 100 to 110 °C°, combustion air from the cooling of the suspended roof of the kiln. The much higher firepower of the newly installed high speed burners, these feature an air exit speed of up to 250 m/s, allows for a much more efficient, as visible in the following kiln temperature curves, and quicker heating of the lower layers and the kiln car plateau. With this assembly the distribution of fuel used in the various zones of the kiln has now changed from about 30% in the preheating zone to about 55% to 60% in the preheating zone. The low efficiency injector burners in the soaking zone, indicated in green in the above engineering drawing, are now used to maintain the temperatures achieved but do not have to heat up the material or the kiln furniture any more.

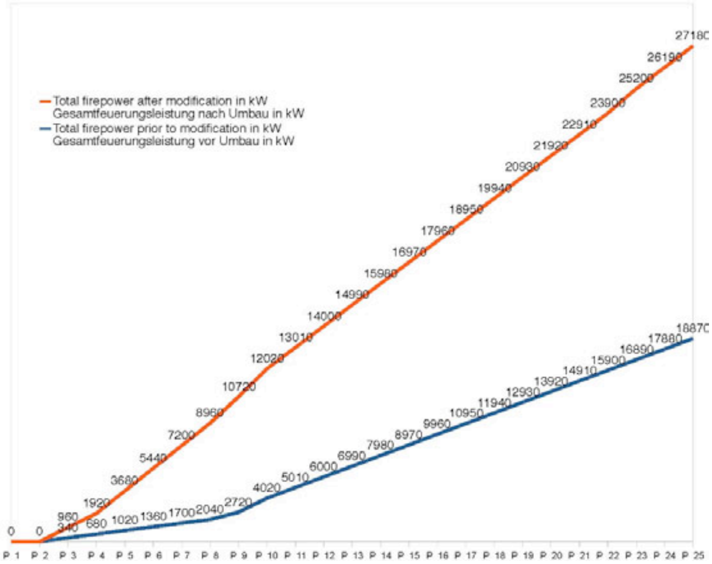
The firing power in the pre-heating zone has increased considerably as pictured in Figure 67 and 68 below:

Fig. 67: Installed fire power old ./. new - single groups of burners



This modification hence resulted also in a change to the total firepower of the kiln that increased considerably over the one previously installed:

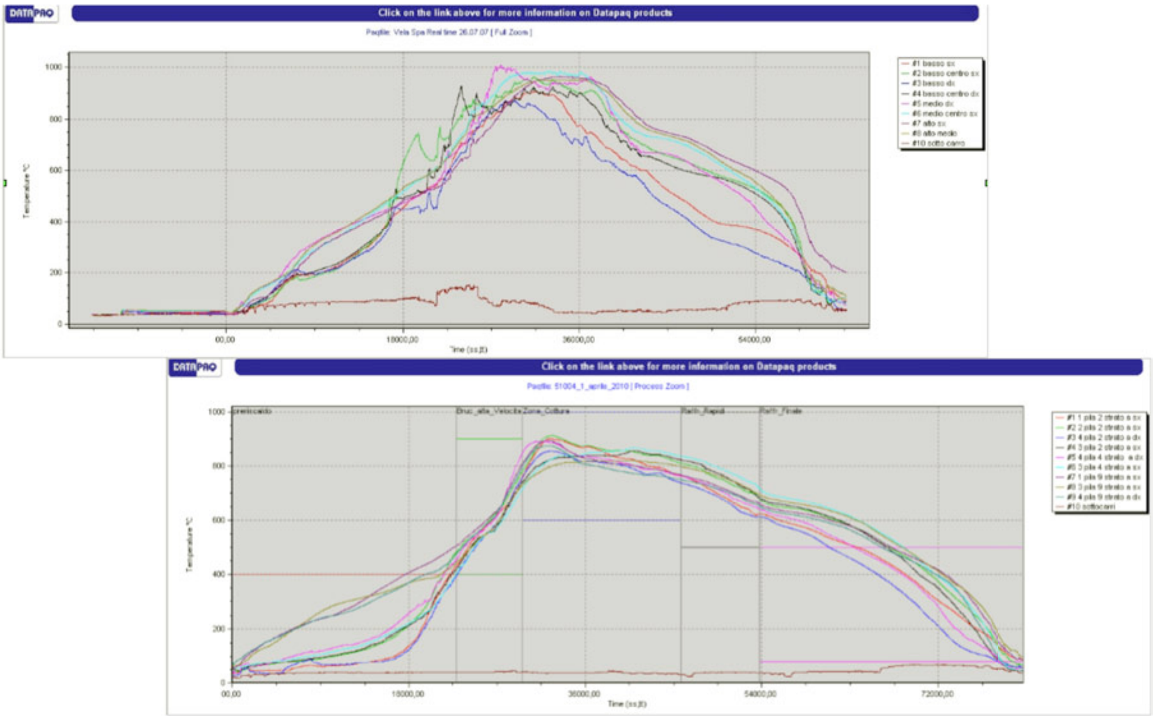
Fig. 68: Installed fire power old ./. new - total



With the previous assembly installation of groups of burners, in this case so called side-burners, occurred at a slightly earlier position than with the actual assembly albeit firepower being much smaller. This had the effect, that the kiln car plateau and the lower layers of brick have not been heated properly requiring the relatively inefficient injection burners of the soak zone to bring the lower layers and the kiln car plateau up to temperature. The side burners have been completely dismantled.

The efficiency of the modifications is explained by the the following two kiln temperature curves. The first one made prior to the modification, and the second once the current modifications had been installed. The temperature profiles have been adjusted for duration of the process, i.e. same

Fig. 69: Datapaq kiln temperature curves VELA S.p.A. Borgonato plant



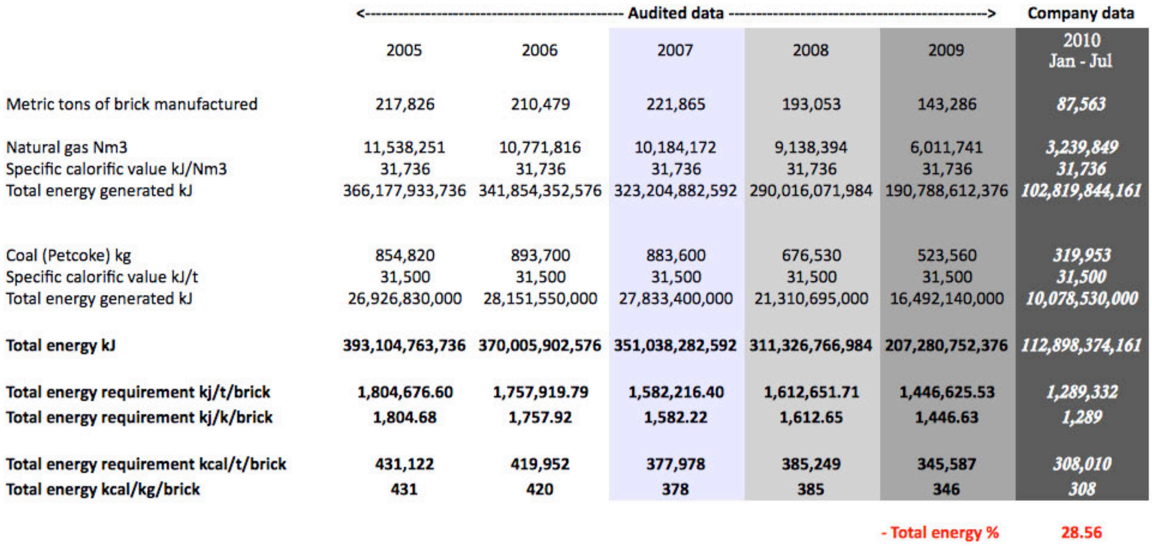
While in the first curve the temperature profile shows extreme temperature differences between the various probes set in the stack of brick traveling through the kiln, the second curve shows far more stable behavior. The second temperature curve however indicates a lack of homogenization of the temperatures in the first zone of the kiln. This problem is currently, summer 2011, addressed. A two speed high pressure recirculation system is installed in the kiln in the zone where the non acceptable temperature differences are found.

Another problem that shows on the second temperature curve is the peak at the beginning of the soaking zone. This peak is due to an injection of outside air as combustion air and hence an increase in the oxygen content of the kiln atmosphere. This leads to combustion of organic, carbonized matter in the feed and hence to a release of energy. This problem will be addressed by connecting the groups of burners where this phenomenon become apparent to the low temperature carbonization gases recirculation system.

The far better uniformity of the temperatures in the soaking zone allowed to lower the overall firing temperatures from 920 °C in 2005 to the 780°C / 800°C, depending on product and push rate, used today. When comparing the two temperature curves it becomes quickly evident, that a certain percentage of the brick in the kiln had been fired at such temperatures even before the modification. This brick however was not up to standards.

The results in energy savings obtained are summarized in the below Table 83. The data of this table have been, except for 2010, audited by ICMQ under the Italian CO_2 scheme.:

Table 85: Energy savings achieved



	<------------------------- Audited data				------------------------->	Company data
	2005	2006	2007	2008	2009	2010 Jan - Jul
Metric tons of brick manufactured	217,826	210,479	221,865	193,053	143,286	*87,563*
Natural gas Nm3	11,538,251	10,771,816	10,184,172	9,138,394	6,011,741	*3,239,849*
Specific calorific value kJ/Nm3	31,736	31,736	31,736	31,736	31,736	*31,736*
Total energy generated kJ	366,177,933,736	341,854,352,576	323,204,882,592	290,016,071,984	190,788,612,376	*102,819,844,161*
Coal (Petcoke) kg	854,820	893,700	883,600	676,530	523,560	*319,953*
Specific calorific value kJ/t	31,500	31,500	31,500	31,500	31,500	*31,500*
Total energy generated kJ	26,926,830,000	28,151,550,000	27,833,400,000	21,310,695,000	16,492,140,000	*10,078,530,000*
Total energy kJ	**393,104,763,736**	**370,005,902,576**	**351,038,282,592**	**311,326,766,984**	**207,280,752,376**	***112,898,374,161***
Total energy requirement kj/t/brick	**1,804,676.60**	**1,757,919.79**	**1,582,216.40**	**1,612,651.71**	**1,446,625.53**	*1,289,332*
Total energy requirement kj/k/brick	**1,804.68**	**1,757.92**	**1,582.22**	**1,612.65**	**1,446.63**	*1,289*
Total energy requirement kcal/t/brick	**431,122**	**419,952**	**377,978**	**385,249**	**345,587**	*308,010*
Total energy kcal/kg/brick	**431**	**420**	**378**	**385**	**346**	*308*
					- Total energy %	**28.56**

The project,change to the mix design and modifications to the kiln, resulted in audited energy savings of about 29%. Considering all the positive factors,

- lesser price for fuel,
- lesser energy requirements,
- lesser expenses due to the use of waste based feed mixes,

the ton of brick today is manufactured for less than 30 euro net of overheads.

Since 2005 the density of the brick has been reduced form an average of 1,72 kg/l to 1,57 kg/l. Hence for the same weight more brick is manufactured and available for sale. This results in a further financial gain of about 8 to 9%.

8.3 Continuation - other projects

The extensive research in the application of renewable fuels in the brick industry has allowed to initiate a CDM Clean Development Mechanism Project for SBBC Societè Briqueterie Bati Chouia under the UNFCC United Nations Framework Convention on Climate Change program. This project is a first of kind (308).

8.4 Conclusion

The results of the research and development work at Ziegel Gasser Mattoni GmbH S.r.l., both in raw materials substitution and integration as well as for process technologies, are being transfered and upscaled to larger sized brick plants with similar impacts, substantial reduction of production costs, as observed at Ziegel Gasser Mattoni GmbH S.r.l..

Utilization of alternative forms of energy has not found, except for an occasional utilization of olive and peaches kernels waste as a fuel by SBBC within the CDM project (309- enclosed in Appendix V), other applications. The current, 2010, low product prices situation might bring a change to that.

A comparative study of the possible impacts on a feed of a large scale brick plant when using a part substitution mix based on sewage and and cooling water treatment sludge has been carried out by the IZF, report KT 3836 enclosed in Appendix VI, for Recuperi Industriali. The results of the report clearly indicate the suitability of the Recuperi mix as an addition to the quarried Wienerberger Bubano plant clay. This IZF report attributes to the Recuperi Industriali / quarried clay Wienerberger Bubano mix good thermal conductivity properties and does not see any reason for not using this mix. This comprehensive third party analysis of the mix is certainly an indication that the know-how gained from research and development work done is applicable to the industry in general.

Appendix I

A South Tyrolean Case Study: Mattoni Gasser Ziegel GmbH S.r.l.

Product development

Brick manufactured in Germany and Austria is usually of higher quality than brick manufactured in Italy. This is mainly due to a much improved technological level. Another reason is certainly, that the market share of brick in the German language countries is much smaller, only around 40 to 45%, than in Italy where the market share is almost 95%. Competition with other wall building products force an innovation cycle upon the German language brick industry that was never felt in Italy, only in South Tyrol. This due to the geographic and language vicinity/affinity of the region.

Since 1990 Ziegel Gasser Mattoni GmbH S.r.l. never got to really control the quality problems, for a lack of technical know-how, that afflicted it mainly caused by uncontrolled use raw materials and dubious choice, even if revenue generating, of waste materials. As waste materials chromium plating and galvanizing sludges, that resulted in poor compressive strength and multi colored efflorescences, have been used.

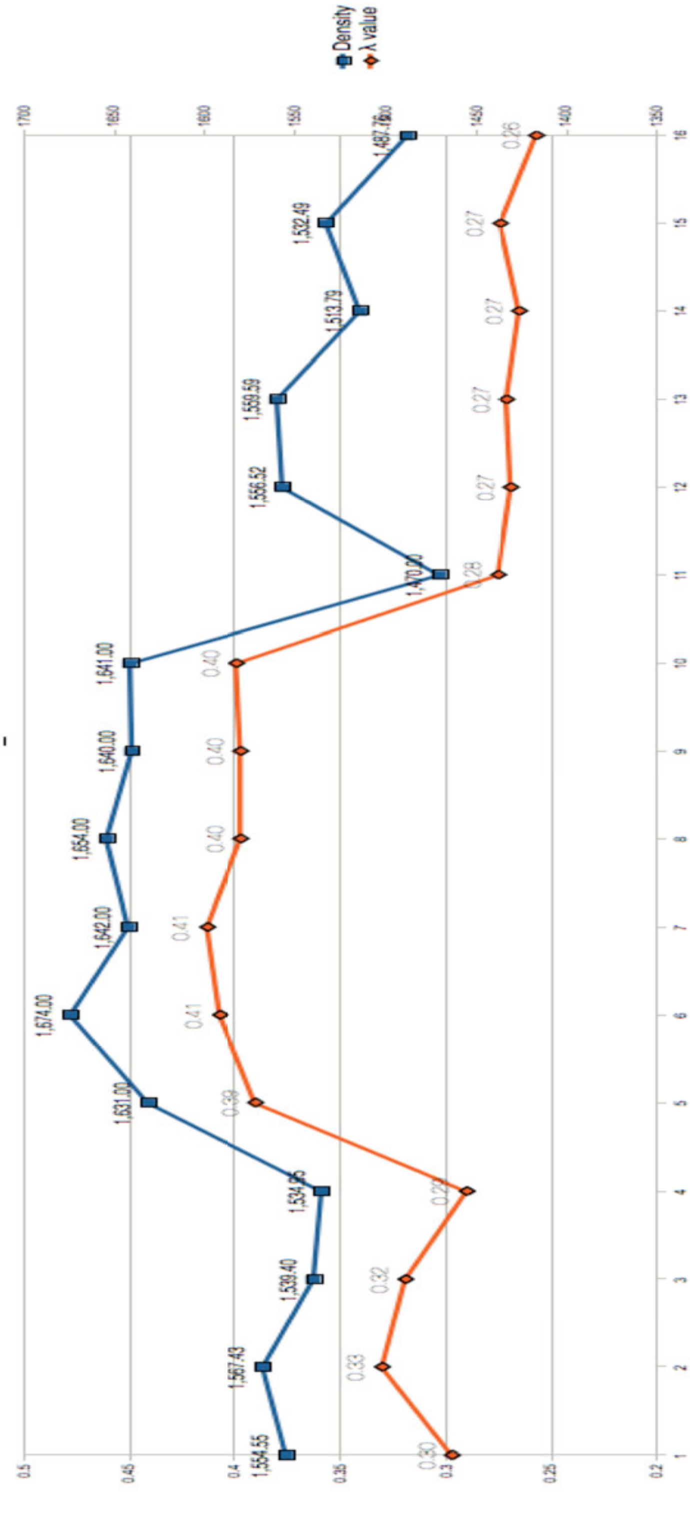
Fig. 70: Ziegel Gasser Mattoni GmbH S.r.l. brick with de-coloration on visible surface

Compared to imported brick, the Ziegel Gasser Mattoni GmbH S.r.l. products featured a poor dimensional quality, firing and drying cracks, uneven surfaces and surface decolorising. As a consequence the product rated very poorly in relation to the imported brick and was only able to command a low selling price.

The strong competition from brick manufacturers from Austria and Germany offering thermal insulation bricks forced Ziegel Gasser Mattoni GmbH S.r.l. to come up with such a brick on his own. The bricks from Austria and Germany are usually sold for a 36.5 cm wall thickness whereas in Italy a 38 cm wall thickness is common.

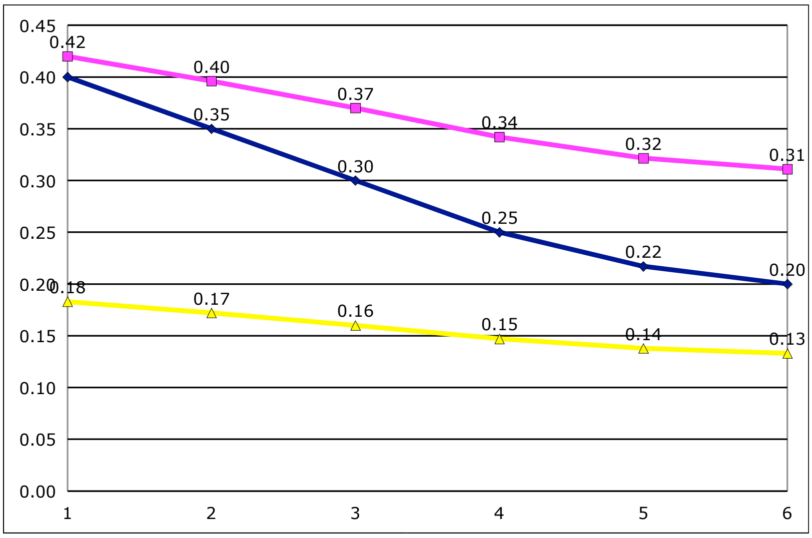
Thermal conductivity vs. material density data from a great number of tests are given in Figure 70 following page:

Fig. 71: Density ./. λ_{brick} value of various mixes



The density to be manufactured in order to achieve the thermal insulation results desired was determined to be for the 38 cm wall thickness block:

Fig. 72: Density ./. Λbrick value for the 38 cm wall thickness
Ziegel Gasser Mattoni GmbH S.r.l. block



In order to obtain the desired thermal conductivity and hence product thermal insulation values it was determined that a material density of less or equal to 1.257 kg/l would have to be obtained. This low density was forced by a number of factors:

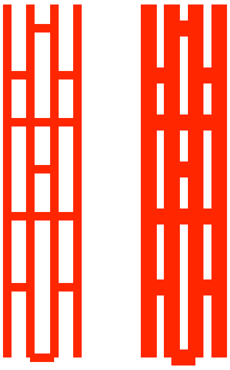
- A bloc manufactured to Italian regulations requires a minimum web thickness of 7 mm and wall thicknesses of 10 mm compared to the 2 to 4 mm web and wall width of Austrian and German blocs.
- The allowed percentage of voids for an Italian bloc must not exceed 47% whereas German and Austrian thermal insulation blocs feature a volume of voids in the range of 55% to 65%.

Table 86: Technical requirements imposed by local standards

	Germany / Austria	Italy UNI 8942
Net minimum compressive strength N/mm²	6	7
Minimum internal wall thickness in mm	None	7
Minimum external wall thickness in mm	None	9
Maximum percentage of voids in % of total surface	None	45 (+/- 2)

This results in a great advantage for the German or Austrian block as these can be manufactured, due to the higher percentage of voids and lower web thicknesses allowed, at a far higher material density for the same apparent block density.

Fig. 73: Typical web thicknesses of German / Austrian and Italian thermal insulating bricks



The above sketch shows how a German or Austrian load bearing brick, left, and a load bearing brick to Italian standards, right, would eventually look.

Ziegel Gasser Mattoni GmbH S.r.l. had no possibility to counter this invasion by starting production of an “imitation brick” but had rather to follow other roads: a thermal insulation brick not based upon a clever design of voids but rather on a novel feedstock.

A technical comparison between the Ziegel Gasser Mattoni GmbH S.r.l. thermal insulation and the German or Austrian thermal insulation bricks is given in Table 87:

Table 87: Product comparison table

Description	Wall thickness 36.5 / 38 cm		
	Standard Gasser brick	ℓ 0,14 DACH averaged	ℓ 0,14 Gasser
Wall thickness	38.00	36.50	38.00
Unit weight kg	19.50	12 .00- 14.00	15.50
R [m^2K/W] wall finished	2.20	2.71	2.71
Thermal accumulation [(kJ / $m^2 \cdot K$)]	> 300	240	265
Sound insulation Rw'R (dB)	> 45	< 41	> 43
Compressive strength (average (least) N/mm^2	14.0 0/ 10.00	7.50 / 6.00	9.00 / 7.50

The 38 cm λ_{brick} 0,14 wall thickness block was later improved with a particular design with varying web thicknesses to achieve an even better thermal insulation value: λ 0,12. This bloc became one of the most successful products in the Ziegel Gasser Mattoni GmbH S.r.l. product history due its competitive price compared to products from Germany and Austria it was sold widely.

Brick for wall thicknesses of 30 cm and 35 cm was also manufactured by Ziegel Gasser Mattoni GmbH S.r.l. to the same technical and quality standards.

Appendix II

A South Tyrolean Case Study: Mattoni Gasser Ziegel GmbH S.r.l.

Comparative study on breathable silica

In late 2004 the discussion about the undeniable health risk of breathable silica intensified. The author decided, especially in consideration of the high percentage of waste used in the bricks manufactured, to benchmark a Ziegel Gasser Mattoni GmbH S.r.l. brick against a brick by another manufacturer. A comparative study was made.Tests have been made cutting a brick with the usual machinery, a wheel cutter, available on a construction site.

Fig. 74: Dry cutting of brick with a wheel cutter

The breathable fraction of the brick cut that has been analyzed, contains particles from the grinding disk used to cut the bricks. The increase in barium oxides and zirconium, materials used in the production of cutting or grinding disks, in both samples leaves way for this supposition. A slight increase in the silica content is also measured. The reason why of the increase in the chromium concentration in the Industria Laterizi Giavarini S.p.A. sample and of fluoride in the Ziegel Gasser Mattoni GmbH S.r.l. sample have not been investigated.

The Ziegel Gasser Mattoni GmbH S.r.l. product was benchmarked against a Industria Laterizi Giavarini S.p.A. product:

Table 88: Solids / breathable dust Ziegel Gasser Mattoni GmbH S.r.l. / Industria Laterizi Giavarini S.p.A. bricks

Impact category		Unit	Fired Giavarini brick	Giavarini breathable fraction released on dry cutting	Fired Gasser brick	Gasser breathable fraction released on dry cutting
Oxides						
Aluminum oxide	Al_2O_3	% dry matter	13.70	12.10	14.30	14.60
Sulfur trioxide	SO_3		0.30	0.50	0.80	0.80
Antimony oxide	Sb_2O_3	mg/kg	< 1.00	< 1.00	< 1.00	2.00
Barium oxides	BaO		900.00	1,400.00	850.00	1,000.00
Boron trioxide	B_2O_3		1,950.00	1,750.00	5,800.00	6,400.00
Calcium Oxide	CaO	% dry matter	13.00	11.40	10.80	10.70
Iron oxide	Fe_2O_3		5.10	4.90	6.70	6.60

Impact category		Unit	Fired Giavarini brick	Giavarini breathable fraction released on dry cutting	Fired Gasser brick	Gasser breathable fraction released on dry cutting
Phosphorus Pentox.	P_2O_5		0.14	0.10	0.56	0.60
Magnesium oxide	MgO		3.20	2.50	2.70	2.70
Manganous oxide	MnO		0.10	0.08	0.11	0.11
Lead oxide	PbO	mg/kg	22.00	22.00	36.00	38.00
Potassium oxide	K_2O	% dry matter	2.50	2.40	2.70	2.60
Silica	SiO_2		59.80	60.90	52.90	54.70
Sodium oxide	Na_2O		1.00	0.90	1.80	1.60
Titanium dioxide	TiO_2	mg/kg	6,200.00	5,900.00	9.400,00	9,600.00
Zinc oxide	ZnO		105.00	270.00	180.00	190.00
Zirconium oxide	ZrO_2		320.00	370.00	270.00	310.00
Heavy metals						
Arsenic	As	mg/kg	8.00	10.00	17.00	17.00
Cadmium	Cd		< 1.00	< 1.00	< 1.00	< 1.00
Σ Chromium	Cr		155.00	205.00	115.00	115.00
Mercury	Hg		< 1.00	< 1.00	< 1.00	< 1.00
Nickel	Ni		110.00	100.00	87.00	83.00
Copper	Cu		28.00	38.00	46.00	38.00
Selenium	Se		< 1.00	< 1.00	< 1.00	< 1.00
Lead	Pb		n.a.	n.a.	n.a.	n.a.
Zinc	Zn		n.a.	n.a.	n.a.	n.a.
Other						
Chlorate		mg/kg	< 50.00	< 50.00	< 50.00	< 50.00
Lithium Oxide			185.00	190.00	190.00	195.00
Strontium			450.00	410.00	450.00	460.00
Fluorite			2,200.00	1,900.00	1.050.00	2,000.00

The Ziegel Gasser Mattoni GmbH S.r.l. product did not show results different from a brick made without the addition of waste materials. It can therefore be safely assumed that the utilization of the wastes in substitution and addition does not increase the risk of breathable fractions released by the brick when dry cutting. Ziegel Gasser Mattoni GmbH S.r.l., however, considering the results and the breathable silica risks clearly evidenced, adopted a policy of labeling its packaging with a symbol, the rightmost one, discouraging dry cutting of bricks and requiring the use of appropriate safety measures.

Fig. 75: Packaging - rear side

This type of labeling was deemed to be non intrusive and unlikely to damage the image of the brick product. Ziegel Gasser Mattoni GmbH S.r.l. is the only manufacturer in Europe who decided to adopt such labeling.

Appendix III

A South Tyrolean Case Study: Mattoni Gasser Ziegel GmbH S.r.l.

EPD – comparative study of results of two different ISO compliant Environmental Product Declarations General EPD information

Ziegel Gasser Mattoni GmbH S.r.l. has been the first hollow clay brick manufacturer in Europe to have his products company specifically covered by an Environmental Product Declaration. As the SWEDAC program was the then Italian Environmental Authorities program of choice, a declaration according to this system had been envisaged and, second declaration assigned in Italy, obtained. Ziegel Gasser Mattoni GmbH S.r.l. is still the only brick manufacturer to be certified under this system. Many countries have schemes for the declaration of environmental information such as INIES in France, AUB in Germany, the BRE Environmental Profiles in the United Kingdom, MRPI in Netherlands, RTS Format in Finland and SIA Deklarationsraster in Switzerland. All of these are different and this fact makes the results from one country and indeed from one manufacturer difficult to compare with those of any other as demonstrated later in this chapter.

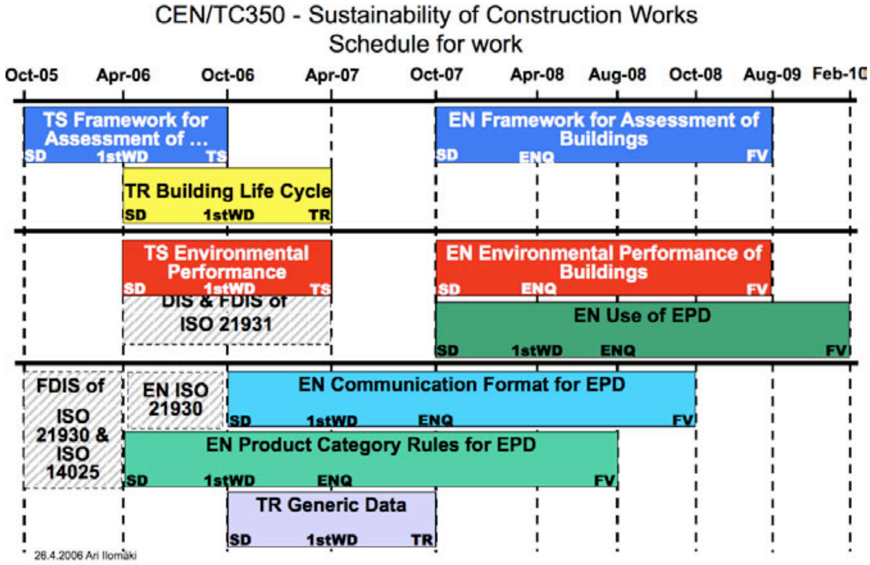
In the preparation of an ISO compliant EPD certain standards must be met and observed: These are ISO 14020 establishing guiding principles for the development and use of environmental labels and declarations. It is intended that other applicable standards in the ISO 14020 series be used in conjunction but it is not intended for use as a specification for certification and registration purposes. ISO 14021 is intended to regulate type II environmental labels such as, for example, “100% recycled paper”, specifies requirements for self-declared environmental claims made by manufacturers, importers, distributors, retailers or anyone else likely to benefit from such claims. ISO 14024 is for type I environmental labels, a “seal of approval” label as the “blue angel” is a typical example, are multi-criteria third-party programs that award environmental labels to products meeting a set of requirements predetermined arbitrarily by the program operator. ISO 14025 type III environmental declarations, EPD's, are principally intended to benefit business to business communication. They are more and more used in business to consumer communication as well, by enabling potential purchasers to make comparisons between products fulfilling the same function. Type III environmental declarations provide quantified environmental information about products, using predetermined parameters based on the ISO life-cycle assessment series of standards. Additional environmental information, such as the impact on biodiversity, instructions and limits for efficient use, or hazard and risk assessment on human health and the environment, among others, is given where relevant. Type III environmental declarations are verified by an accredited verification organization. ISO 14025:2006 establishes the principles and specifies the procedures for developing Type III environmental declaration programs and Type III environmental declarations. It specifically establishes the use of the ISO 14040 series of standards in the development of Type III environmental declaration programs and Type III environmental declarations.ISO 14025:2006 establishes principles for the use of environmental information, in addition to those given in ISO 14020:2000

ISO 14040, LCA Principles and framework, and ISO 14044, LCA Requirements and guidelines, are used in the preparation of LCA. The ISO 14041LCA Goal and scope definition and life-cycle inventory analysis, ISO 14042 LCA Life-cycle impact assessment and ISO 14043 LCA Life-cycle interpretation have become obsolete with the publication of the 2006 standards.

Another important factor in LCA is the characterization of toxic chemicals with relevance to human exposure based on the potential human toxicological effects expressed as critical volume i.e. the volume of a certain media required to absorb a specific emission without resulting in adverse effects. The location where a probable exposure might occur (indoor versus outdoor) and inter-media transport of substances is to be considered. Among the substances to consider are nmVOC from road transport, heavy metals (cadmium, lead, mercury etc.), nitrous oxides (No_x), sulfur dioxide (SO_2), volatile organic compounds (VOC), chlorinated organic compounds, persistent organic pollutants (POP), particulate matter (PM_{10}) This is expressed as “human toxicity” factor.

In 2005 the European Committee for Standardization started, with CEN/TC 350 Sustainability of Construction Works an initiative targeted, with an end date set initially for 2010, for the unification of the various ISO compliant EPD schemes in existence.

Fig. 76: CEN/TC 350 working plan



The risk of the work of CEN/TC350 is, that various interests delay the work of the unified system leaving ample space for national non standardized schemes to spread and proliferate causing in the end the potential users of the EPD to not trust any more in this instrument. Common and comparable EPD's based on unique PCRs would eliminate trade barriers to trade that otherwise might be, voluntarily or involuntarily, arise. Assessments or comparisons that may be required should be made at the level of of a building sustainability and any assessment should be carried out for the complete entire life cycle of the building and its principal components considering a possible future use beyond the original intended service life and the complete technical and social context of the works.

The differences in the evaluation of the impacts for the same product by schemes that in theory should deliver, both being ISO based, the same result have been object of study. The existing Ziegel Gasser Mattoni GmbH S.r.l. SWEDAC EPD has hence been compared, using the same raw data and functional unit concept, to an EPD prepared under the AUB scheme resulting in some substantial difference in the calculated impacts.

The energy impact results of the AUB scheme are more than 60% lower than according to the SWEDAC scheme.

Table 89: Impacts of resources with energy content in g/t

	SWEDAC (Boustead)		AUB (GaBi)	
	Production	Use	Production	Use
Wood	3,067.00	0.00	0.00	0.00
Biomass	369.70	3.10	0.00	0.00
Waste	450,808.00	0.00	144,832.00	0.00
Sum renewable resources	454,244.70	3.10	144,832,00	0.00
Crude oil	8,469.00	5,510,00	9,791.00	3,118.00
Gas / Condensate	13,009,00	183.60	14,073.00	134.84
Coal	13,344.00	81.40	17,406.00	12.50
Metallurgical coal	253.50	140.00	0.00	1.00
Lignite	0.40	0.10	1,168.00	39.12
Peat	0.00	0.00	0.00	1.00
Uranium	0.09	0.10	0.12	0.00
Sum non-renewable resources	35,075.59	5,915.20	42,438,12	3,306.46
Total impact	489,320.29	5,918.30	187,721.12	3,306.46

This result emphasizes the need for an uniform calculation method. These differences are not acceptable. The scheme operators explain the difference very summarily by difference in the valuation of the wood, sawdust, used and in the valuation of the biomass either as dry or as humid.

Table 90: Difference in impacts for the raw materials flow in g/t[1]

	SWEDAC (Boustead)		AUB (GaBi)	
	Production	Use	Production	Use
Glass fiber scrap	127,670.00	0.00	127,670.00	0,00
Sum renewable resources	127,670.00	0.00	127,670.00	0,00
Bauxite	2.60	1.40	> 0.01	
Sodium chloride[2]	43.50	6.90	95.35	0.00

---

[1] g/t is a common indicator in EPD's, gramms per ton

	SWEDAC (Boustead)		AUB (GaBi)	
Clay	1,061,585.00	0.00	836,100.00	0.00
Fe	629.30	347.50	545.45	0.04
Pb	1.30	2.40	1.09	0.00
Carbonates as Limestone ($CaCO_3$)	23,351.00	72.60	17,599.00	0.93
SiO_2 considered as sand	29.90	0.00	45.13	0.00
Elemental sulfur	2.40	1.30	> 0.01	0.00
Dolomite	7.70	4.20	0.23	0.00
Gravel	102,080.00	1.30	131,384.00	0.00
Olivine	5.90	3.30	-	-
Potassium chloride[1]	2.30	0.00	0.05	0.00
Sandstone	69,599.00	0.00		
Sum non renewable resources	1,257,339.90	440.90	985,770.30	0.97
Total impact	1,385,099.90	440.90	1,113,440.3	0.97

Both models do not consider the wast raw material streams, except for glass fibre, as a renewable stream. The substitution of raw materials with waste materials, such as sewage sludge, ashes and paper sludge, does hence not find any evidence in a reduced impact. Both system operators did not supply information why these substantial waste stream have not been considered as a reduction of the environmental impact of the production process.

A further error is certainly that elements and components already considered in “clay” are once more listed and their impact calculated.

Substantial is the difference in the impact of the utilization phase of the product, the main difference being due to the impact valuation of Fe.

Table 91: Total impacts

	SWEDAC (Boustead)		AUB (GaBi)	
Impact indicator	Production	Use	Production	Use
GWP 100 (fossil) in kg CO_2	120.70	20.00	95.30	10.25
GPW 100 (renewable)in kg CO_2	1,903.30	0.00	264.80	0.00
Acidification in kmol H+	0.11	0.01		
Acidification in in kg SO_2	3,45	0.23	2.94	0.09

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[2] In both declarations the original error of classification of a raw material, indication of liquid sodium silicate (waterglass) as sodium chloride, is repeated.

[1] See remarks previous footnote

	SWEDAC (Boustead)		AUB (GaBi)	
Eutrophication in kg O_2	18.71	1.31		
Eutrophication in kg $PO_4 3-$	0.62	0.04	0.40	0.02
POCP in kg C_2H_4	0.09	0.05	0.19	0.02

The GWP potential of the SWEDAC EPD for biomass is almost 8 times the same value calculated to the AUB EPD scheme. A product certified to the AUB scheme will hence compare far better than a product certified to the SWEDAC system. The differences are explained as:

- The materials cellulose, composted organic material, rendering fat and fruit ashes contribute to the calculation of the GWP100 (biomass);
- GWP100 (biomass) in the SWEDAC EPD system is calculated with a CO_2 emissions factor of 4,44 kg CO_2 per kg biomass, the moisture weight of the materials is taken into account whereas in the AUB EPD system the emissions from the same material are calculated with a CO_2 emission factor of 1,83 kg CO_2 per kg biomass taking into account only the dry matter as a base of calculation;
- The particular fuel situation at Ziegel Gasser Mattoni GmbH S.r.l. required an exception to be made in the AUB EPD scheme as the emissions from the rendering fat used as a fuel had been calculated to be 1,78 kg CO_2 and hence further some of its impacts had been calculated in the GWP 100 (fossil) category. The impact of the use of rendering fat on tGWP100 (fossil) is 41%. The same exception had not been made in the SWEDAC EPD scheme where the fat has been calculated with it's full impact;
- In the SWEDAC EPD system: materials which contributes less than 0,5% of the total weight can be omitted / no omission can be applied for hazardous substances / all omissions must be documented and justified whereas in the AUB EPD system processes which contributes less than 1% of the total weight and less than 1% to the primary energy demand can be omitted. On the output side flows contributing less than 1% to a impact category shown in the result can be omitted / the total amount of omitted processes must be less than 5% / considered values should be annual average values / assumptions for missing processes are allowed / all assumptions and omissions must be documented;
- Mass criteria in the SWEDAC EPD system will be used in terms of partitioning the system inputs and outputs / economic allocation criteria is excluded whereas in the AUB EPD system allocations should be avoided / if allocation is necessary the criteria has to reflect the purpose of the process / economic allocation criteria are possible;
- Both EPD systems allow cut-off methods for so called open-loop recycling into the life cycle of another product. In the AUB EPD scheme the definition of waste is very specific as the prerogative is for them to have a negative market value (AUB).

And for the inventory, generic, data:

Table 92: Generic inventory data

	SWEDAC	AUB
GWP	Kg $CO_{2\text{-equiv}}$ (IPPC 1996)	Kg $CO_{2\text{-equiv}}$ (IPPC 2001)

	SWEDAC	AUB
ODP	Kg CFC $11_{\text{-equiv}}$ (Nordic Guidelines on LCA 1995)	Kg CFC $11_{\text{-equiv}}$ (WHO 1995)
AP	Mol H- $_{\text{-equiv}}$ (no reference)	Kg $SO_{2\text{-equiv}}$ (CML 2001)
EP	Kg $O_{2\text{-equiv}}$ (Nordic Guidelines on LCA 1995)	
POCP	Kg $C_2H_{4\text{ -equiv}}$ (Derwent et al. 1998)	Kg $C_2H_{4\text{ -equiv}}$ (CML 2001)

Two conclusions can be drawn from these data:

- The existing schemes are in no position to promote, for better or worse, any given product;
- A unified, European wide and unique scheme and comparable scheme is needed at the earliest opportunity to stop unfair utilization and manipulation of impact data.

Lacking standardization, the current EPD schemes are not a useful tool to demonstrate the environmental impact of any given product. Their use requires, especially if products are used that have obtained classification under different schemes, a detailed knowledge of the methods and rules used in determining the environmental impact figures and these are not always available. From this point of view the Ziegel Gasser Mattoni GmbH S.r.l. EPD certifications are a useful tool to demonstrate changes in the environmental impact but they have only limited value when using them to benchmark the product. Some benchmarking, using data published in the DACH study, has been made. Given the above, the intrinsic value and usefulness of such benchmarking must be considered to be of limited value and only a rough indication of “what could be”.

Had such information have been available before commencing the EPD project, then it would almost certainly not have been started.

Standards dealing with the environmental impact of buildings and building products, both existing and under development are given in Table 93:

Table 93: ISO TC/207 standards

Standard number	Standard title	Comment
ISO 14001 (EN ISO 14001)	Environmental management systems – specification with guidance for use	These supports the first level of EPD schemes
ISO 14020 (EN ISO 14020)	Environmental labels and declarations – General principles .	
ISO 14021 (EN ISO 14021)	Environmental Labels & Declarations - Environmental Labeling TYPE II – Self Declared Environmental Claims	
ISO 14024 (EN ISO 14024)	Environmental Labels & Declarations - Environmental Labeling TYPE 1 – Guiding Principles and Procedures	
ISO 14025	Environmental labels and declarations - type III environmental declarations	An important reference for the Standards of ISO/TC 59 SC 17 and CEN/TC 350

Standard number	Standard title	Comment
ISO 14040 (EN ISO 14040)	Environmental management - Life Cycle assessment - Principles and Framework	These documents supersedes EN ISO 14040:1997, EN ISO 14041:1998, EN ISO 14042:2000, EN ISO 14043:2000.
ISO 14044 (EN ISO 14044)	Environmental management – Life cycle assessment – Requirements and guidelines	

Standards that are under development or revision in ISO/TC 59 SC 17[1]

Table 94: ISO/TC 59 SC 17 standards

Standard number	Title of Standard	Comments
ISO/DIS15392:2008	Buildings and constructed assets - Sustainability in building construction – General principles	FDIS ballot initiated on 2008-01-15: 2 months comment period.
IISO/AWI TR 21932	Buildings and constructed assets - Sustainability in building construction - Sustainability indicators	Working draft (WD) study initiated 2004-03-08
ISO/FDIS 21930	Buildings and constructed assets - Sustainability in building construction - Environmental declaration of building products	Published on 01/10/2007. Provides principles and requirements for type III EPD's but does not define requirements for type III programs and excludes working environment as this is left not national legislation. Is seen as a complement to ISO 14025. International Standard published – will have to be revised.
ISO/TS 21931	Buildings and constructed assets - Sustainability in building construction - Framework for assessment of environmental performance from buildings	Standard published as a Technical Specification on 19th July 2005. Is to be used in conjunction with the ISO 14000 series. International Standard under revision.
ISO/TS 21932	Buildings and constructed assets - Sustainability in building construction – Terminology	AHG working with ISO/TC 59 SC 2,14,15,17 and CEN/TC 350 to establish a common terminology document. Working draft (WD) study initiated on 2004-03-08)

Table 95: CEN/TC 350 standards (under development)

Standard number	Standard title	Comment
CEN/TC 350 N 82	Sustainability of construction works- Framework for assessment of integrated buildings performance- Part 1: Environmental, Health and Comfort and Life Cycle Cost Performances	The document will become a Technical Specification on approval. Some MS would like to see more emphasis on Health and Comfort and Life Cycle Cost Performances.
CEN/TC 350 N 75	Sustainability of construction works- Assessment of environmental performance of buildings- calculation methods	
CEN/TC 350 N 73	Sustainability of construction works-Environmental product declarations-Product category	

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[1] Situation as per February 2007

Standard number	Standard title	Comment
	rules	

Although, EPD Systems are certainly not to be deemed ideal, they are nevertheless the only means of more or less accurately determining the environmental impact to a wider audience.This is especially the case when substantial amounts of waste are used in substitution of raw materials and this information is to be made public. Appropriate technical documentation is required that emphasizes the positive results and counters effectively the subjective consumer point of view of not “wanting to live in a repository of waste materials”. Between 2000 and 2006, Ziegel Gasser Mattoni GmbH S.r.l. lost two sales for using sewage sludge in its product. On the other hand, brick has been supplied to important projects such as the Media Centre for the 2004 Turin Winter Olympics on the grounds of the reduced environmental impact of the product.

Appendix IV

A South Tyrolean Case Study: Mattoni Gasser Ziegel GmbH S.r.l.

Benchmark data

IV.1 Introduction

An useful tool for benchmarking a production process are the data contained in the European BREF/BAT (310) document. In addition national BREF/BAT documents, such as the Italian (68) can be used. Industry wide statistical data obtained from other sources like, for example, the IZF Institut für Ziegelforschung or the NBRC National Brick Research Center or national trade associations can be used as well. The main indicators for such benchmarking are energy consumption, emissions and use of land, i.e. raw materials, in the brick making operation under review. EPD's, both sector wide and manufacturer specific, can also be used.

The data covering the release of substances to the environment of a built structure are generally similar for all ceramic products but the impact of the associated production process can vary significantly.

IV.2 Use of energy

The energy question is of paramount importance in the brick industry. Usually between 25 and 40 % of the operational expenses of a brick yard are energy related. Most of it is for energy used for firing bricks. The use of renewable or alternative sources of thermal energy (311) is limited to a few select manufactures (Ziegel Gasser Mattoni GmbH S.r.l. in Italy uses rendering fat, vegetable oils (312) (313) and biogas from a pilot plant, Deppe in Germany used or uses recycled lubricants, in Spain, the Netherlands and the UK some manufacturers use gas generated in a landfill sites). The reason for this is the extreme fragmentation of the brick industry .

The energy situation:

Table 96: Development of the percentage of various fuels used in firing heavy clay products (TBE – Tile & Brick Europe – personal communication)

Country	Coal use in %					Oil use in %					Natural gas use in %				
	1960	1975	1990	1995	2001	1960	1975	1990	1995	2001	1960	1975	1990	1995	2001
Austria			2					20	19	15			78	81	85
Belgium	83	4	10	4	2	17	40	7	6	2		56	83	90	96
Germany	77	5	3	3		20	76	17	15		3	19	80	82	
Denmark	68	11	5	4		32	89	9	9				86	87	
France		4	15				56	9	5			40	76	95	
Italy				2				49	19	10			51	79	90
Netherlands	49	2	2	1		51	1	1				97	97	99	
Spain	30	10				50	65	71	67		20	25	29	33	
United Kingdom		50	11	4	3		14	4	2	1		36	85	94	96
Hungary	94	60	26	15		6	8					32	74	85	

Country	Coal use in %					Oil use in %					Natural gas use in %				
	1960	1975	1990	1995	2001	1960	1975	1990	1995	2001	1960	1975	1990	1995	2001
Switzerland			1					63	51	47			36	49	53

The energy required for the ceramic process itself is, depending on the composition of the raw materials, to be found in between 75 and 175 kJ/kg of material. Any other energy supplied is not necessary for the ceramic process itself but lost under one or the other form.

Table 97: Specific Energy Consumption kJ/Kg for the European brick and roof tile industry (TBE – Tile & Brick Europe – personal communication)

	Year 1980 kJ/Kg	Year 1985 kJ/Kg	Year 1990 kJ/Kg	Year 1995 kJ/Kg	Year 2001 kJ/Kg
Austria	2,380	2,090	1,710	1,720	1,650
Belgium	3,300	2,730	2,160	2,370	2,230
Germany	2,430	2,310	1,930	1,630	
Denmark	2,730		2,410	2,670	
France	2,870	2,620	2,760	2,610	
Italy	2,800	2,600	2,100	1,900	1,900
Netherlands	3,630	2,930	2,860	1,700	
Spain	2,380	2,290	2,240	2,180	
United Kingdom	3,580	3,260	2,970	2,800	1,400
Switzerland		2,550	2,620	2,530	2,320

The overall production figures of some TBE member countries offer an idea about the predominant product in this country. Italy, together with Spain for which no data are available, are the largest producers of heavy clay products in Europe. In Italy the market share of blocks for perimeter or divider walls exceeds 90%. No other wall material holds a significant market share.

This particular circumstance has not contributed to the competitiveness of the Italian brick industry that mostly relies on rather obsolete plant. Poor product quality, when compared to blocks manufactured for example in Germany or Austria, is another issue that is being addressed only recently.

Table 98: Tons of production 2003 (‘000)

Country	Facing bricks and pavers	Blocks	Roof tiles	Plants in operation
Austria	19	1,720	121	31
Belgium	1.720	1.265		35
Germany	2,800	5,600,	2,600	153
Denmark	710		50	27

Country	Facing bricks and pavers	Blocks	Roof tiles	Plants in operation
France	359	1,998	2,864	90
Italy	1,316	15,906	1,757	240
Netherlands	2,034			45
Spain[1]	n.d.	n.d.	n.d.	280
United Kingdom	6,980		117	102
Switzerland[2]	n.d.	n.d.	n.d.	n.d.

In Italy, for example, the total production data between 2005 to 2008 dropped from 20.752 million ton to 17,058 million ton or almost 18% (314). In Germany the market shrank by a little less than 8% over the same period (315).

Energy data are not directly comparable as in the different countries the product range manufactured is not comparable. No specific relationship does exist between type of fuel, predominant type of product and energy savings achieved (albeit there is a trend to greater savings mainly in the countries with the highest rate of utilization of gas as fuel and where the predominant product are blocks). In firing roof tiles current technology still requires a relative large percentage of the employed energy to be used to heat kiln furniture and for facing bricks and pavers usually higher firing temperatures than for blocks are required. The overall picture however is non homogenous and leads to the conclusion that the use of energy is very much still dealt with at single plant level rather than from a global perspective.

The average energy consumption today is, as from papers internal to the IZF – Institut für Ziegelforschung, to be estimated to be 1,316 kJ/kg brick with the best marks at below 450 kJ/kg brick.

Data are to be found in the following ranges:

Table 99: Energy balance of tunnel kiln (data from own measurements and from literature)

Process	Energy requirement
Ceramic transformation	75 to 175 kJ/kg
loss due to kiln car	110 to 300 kJ/kg
Flue gas loss	65 to 600 kJ/kg
Kiln insulation	10 to 190 kJ/kg
Cooling air	175 to 950 kJ/kg
Transformation of carbonate minerals	15 kJ/kg carbonate content in % of total mass fired

Improvements might be made in the design of kiln cars, burners and the insulation of the kiln itself. It is also possible to reduce firing temperatures by unifying them across the section of the kiln.

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[1] Spain does not make available any production data to TBE.

[2] Switzerland publishes data for volume and wall area but not for quantity.

IV.3 Emissions

The CO_2 emissions of brick plants within the EC, are, with the exception of Italy where almost all plants have been excluded from the scheme until 2012 due to a very industry friendly interpretation of the allocation threshold rules, subject to the EC emissions trading directive EU ETS (see also: Climate Change Levy CCL agreements in the UK). The adoption of the EU ETS does impose an upper limit on a manufacturer's generation of process CO_2, combined material conversion and combustion emissions, meaning that once reached, the only option will be to buy CO_2 credits at the prevailing market price, or cease production.

In addition to the energy related emissions there are also 'pollution' emissions that the brick industry has for some years been required to minimize, namely those of hydrogen fluoride (HF). HF occurs naturally in the clay minerals used to manufacture bricks. When heated to above 800°C the breakdown of the clay minerals releases the HF into the kiln atmosphere where it can either react with other minerals found in the bricks, such as lime, or is emitted along with the other combustion exhaust gases via the stack, and then to air.

Brick plants that currently have high HF levels in the clay, are required to 'scrub' the exhaust gases prior to being discharged to the air. The current permitted emission limit is 10mg/m3. The majority of manufacturers are required to use methods such as 'end of pipe' solutions, typically limestone scrubbers, to comply with this level of emission.

Table 100: Emission data Italian and European brick industry normalized at 18% O

Substance	Unit	Italy			Europe	
		Minimum value	Average value	Maximum value	Minimum value	Maximum value
Dust	mg/Nm^3	0.4	12.1	39.0	1	30
NO_x as NO_2		4.0	48.5	94.0	10	550
SO_x as SO_2		-	104.7	420.0	5	3,200
Fluoride as HF			2.1	5.0	1	350
Chloride as HCl		0.4	9.2	15.0	1	200
Total organic		0.3	11.4	29.5	25	50
Ethanol average	mg/kg brick	No data for Italy			3.10	no limit
Benzene	mg/Nm3		1.6		1	65
Methanol average	mg/kg brick	No data for Italy			5.70	no limit
Phenol	mg/Nm3		1.0	4.0	5	100
Formaldehyde		No data for Italy			1	20
Aldehyde (S C1 – C4)					1	180
Carbon monoxide		102.0	292.5	512.0	< 7	< 1,500

Data from different countries are not directly comparable as very frequently the exact reference oxygen value is not indicated for the published data.

- sulfur dioxide and sulfur compounds are closely related to the sulfur content of the raw materials, reactants used and the fuel employed. Whereas natural gas is almost free from sulfur, bio- or landfill gas can however feature considerable percentages, due to the bacterial conversion of proteins contained in the substrate, of sulfur. In case petrol coke or coal is used sulfur emissions can be, if no gas treatment does exist, exceed the threshold values. The raw material or waste used can contain sulfur in the form of pyrite (FeS_2), gypsum and other sulphate, and organic sulfur compounds. Whereas sulfur is released into the environment, the reaction products are retained within the brick body.
- Nitrogen oxides and other nitrogen compounds are generated by “fixation”, a illustrative term used in the European BREF for the ceramic industry, of nitrogen and oxygen from the combustion air usually in the hot burner flames when the general kiln temperature is too low or at kiln temperatures above 1,200 °C.
- Carbon monoxide and carbon dioxide usually derive from organic matter contained in the clay body to be fired especially under low oxygen firing condition. Reaction of carbon contained in the clay body with carbon dioxide, CO_2 released by thermal dissociation of alkali and earth alkali carbonate minerals such as calcium or magnesium during firing is another source of carbon monoxide and dioxide.
- Volatile organic compounds are released by organic matter contained in the clay used itself or any form of added organic substances. Carbonization may occur with the release of complex and various VOCs.
- Dioxin and furan are usually not considered to be an issue in the brick industry. Albeit measurements by the author confirm their presence in the flue gas in measurable quantities even if the values are within the expected limits of about 0,1 ng TE/m^3 (316). In the presence of high chloride contents in the body, due to the clay itself or brick body density reducing agent agents as, for example, chloride bleached paper or recycled styrofoam, this valued could be exceed. Dioxins are generally released from the combustion of carbon contained in the brick body in the normal production process of especially pored bricks at the temperature range of 250 °C to 350 °C in the preheating zone of the kiln whenever excess CO_2 is available (317).
- Metals and metallic compounds are generally of limited concern, except if the fuel already contains such substances.
- The emission of chlorine and chlorine compounds are due to the chlorine content in the clay itself, chlorinated mixing water, decomposition of chlorine rich mineral salts usually at temperatures > 850°C and of organics in the temperature range 450°C to 550°C.
- As with chlorine, the emission of fluorine is caused by fluorosilicates of various kind present in the clay itself by decomposition at temperatures between 550° and 750°C depending on the mineral form and by decomposition of CaF_2 at temperatures in excess of 900 ºC - due to the firing temperatures common today a not very frequent phenomenon.

Emissions to water are limited as the water contained or added to the ceramic body is evaporated during the production process. Waste water is mainly generated by equipment cleaning and, if such equipment is used, by wet flue gas scrubbers.

Appendix V

A South Tyrolean Case Study: Mattoni Gasser Ziegel GmbH S.r.l.

Normative and legislative situation in the European Community

Environmental legislation[1] within the European community is delegated to the EC. The single countries however retain ample powers to further legislate based on common EC legislation: What is allowed in one country is not necessarily allowed in another EC member country:

Table 101: Overview of regulatory and normative aspects withing the EC

Sustainable development	Communication from the Commission of May 15, 2001 "A Sustainable Europe for a Better World: A European Union Strategy for Sustainable Development" (Commission's proposal to the Gothenburg European Council). Communication from the Commission of December 13, 2005 on the review of the Sustainable Development Strategy - A platform for action 2009 Review of the EU Sustainable Development Strategy - Presidency Report Sustainable development in the European Union - 2009 monitoring report of the EU sustainable development strategy - Eurostat Statistical books Commission of the European Communisties - Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the regions. - Mainstreaming sustainable development into EU policies: 2009 Review of the European Union Strategy for Sustainable Development
Waste	Directive 2006/12/EC of the European Parliament and of the Council of April 5, 2006 on waste. Council Directive 91/689/EEC of December 112, 991 on hazardous waste. 2000/532/EC - Commission Decision of May 3, 2000 replacing Decision 94/3/EC establishing a list of wastes pursuant to Article 1(a) of Council Directive 75/442/EEC on waste and Council Decision 94/904/EC establishing a list of hazardous waste pursuant to Article 1(4) of Council Directive 91/689/EEC on hazardous waste. Council Regulation (EEC) No 259/93 of February 1 (1993 on the supervision and control of shipments of waste within, into and out of the European Community. 93/98/EEC: Council Decision of February 1 (1993 on the conclusion, on behalf of the Community, of the Convention on the control of trans -boundary movements of hazardous wastes and their disposal (Basel Convention). Commission Regulation (EC) No 1547/1999 of July 12 (1999 determining the control procedures under Council Regulation (EEC) No 259/93 to apply to shipments of certain types of waste to certain countries to which OECD Decision C(92)39 final does not apply (Text with EEA relevance) determining the control procedures under Council Regulation (EEC). Regulation (EC) No 1013/2006 of the European Parliament and of the Council of June 14, 2006 on shipments of waste.
Noise	Directive 2002/49/EC of the European Parliament and of the Council of June 25, 2002 relating to the assessment and management of environmental noise.
Air pollution[2]	Directive 2008/50/EC on ambient air quality and cleaner air for Europe merging most of existing legislation into a single directive (except for the Fourth Daughter Directive) with no change to existing air quality objectives and new air quality objectives for PM2.5 (fine particles) including the limit value and exposure related objectives – exposure concentration obligation and exposure reduction target. With this directive the possibility to discount natural sources of pollution when assessing compliance against limit values has been introduced together with the possibility for time extensions of three years for (PM10) or up to five years fo (NO_2, benzene) for complying with limit values, based on conditions and the assessment by the European Commission. Council Directive 96/61/EC of September 24 (1996 concerning integrated pollution prevention and control (and subsequent amendments and integrations). Council Directive 1999/30/EC of April 22 (1999 relating to limit values for sulfur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air amended

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[1] For completeness commission communications are included.
[2] Legislation pertinent to the transport sector is omitted from this ovetview.

	by 2001/744/EC: Commission Decision of October 17, 2001 amending Annex V to Council Directive 1999/30/EC relating to limit values for sulfur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air. Directive 2001/81/EC of the European Parliament and of the Council of October 23, 2001 on national emission ceilings for certain atmospheric pollutants. Council Directive 85/203/EEC of March 7 (1985 on air quality standards for nitrogen dioxide. Regulation (EC) No 2037/2000 of the European Parliament and of the Council of June,2 9 2000 on substances that deplete the ozone layer 81/462/EEC: Council Decision of June 11 (1981 on the conclusion of the Convention on long-range trans-boundary air pollution. 2001/379/EC: Council Decision of April 4, 2001 on the approval, on behalf of the European Community, of the Protocol to the 1979 Convention on Long-range trans-boundary Air Pollution on Heavy Metals. 2006/507/EC: Council Decision of October 14, 2004 concerning the conclusion, on behalf of the European Community, of the Stockholm Convention on Persistent Organic Pollutants. Directive 2003/87/EC of the European Parliament and of the Council of October 13, 2003 establishing a scheme for greenhouse gas emission allowance trading within the Community and amending Council Directive 96/61/EC. Directive 2001/80/EC of the European Parliament and of the Council of October 23, 2001 on the limitation of emissions of certain pollutants into the air from large combustion plants. Council Directive 88/609/EEC of November 24 (1988 on the limitation of emissions of certain pollutants into the air from large combustion plants. Council Directive 94/66/EC of December 15 (1994 amending Directive 88/609/EEC on the limitation of emissions of certain pollutants into the air from large combustion plants. Council Directive 89/369/EEC of June 8 (1989 on the prevention of air pollution from new municipal waste incineration plants . Directive 2000/76/EC of the European Parliament and of the Council of December 4, 2000 on the incineration of waste . Council Directive 94/67/EC of December 16 (1994 on the incineration of hazardous waste . Directive 2001/81/EC of the European Parliament and of the Council of October 23, 2001 on national emission ceilings for certain atmospheric pollutants . Directive 2002/3/EC of the European Parliament and of the Council of February 12, 2002 relating to ozone in ambient air . Council Directive 1999/32/EC of April 26 (1999 relating to a reduction in the sulfur content of certain liquid fuels and amending Directive 93/12/EEC .
Water[1]	Groundwater Directive 2006/118/EC Water Framework Directive (WFD)- Directive 2000/60/EC of the European Parliament and of the Council of October 23, 2000 establishing a framework for Community action in the field of water policy and Directive 2006/118/EC of the European Parliament and of the Council of December 12, 2006 on the protection of groundwater against pollution and deterioration. COUNCIL DIRECTIVE of December 12 (1991 concerning the protection of waters against pollution caused by Nitrate from agricultural sources (91/676/EEC). DIRECTIVE 2006/118/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of December 12 , 2006 on the protection of groundwater against pollution and deterioration. Directive 2006/11/EC of the European Parliament and of the Council of February 15 , 2006 on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community (Codified version). Council Directive 80/68/EEC of December 17 (1979 on the protection of groundwater against pollution caused by certain dangerous substances
Nature and biod-	Communication from the Commission - Halting the loss of biodiversity by 2010 - and be-

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[1] Legislation non pertinent to use of water in industry is omitted if not of general interest.

iversity	yond - Sustaining ecosystem services for human well-being {SEC(2006) 607} {SEC(2006) 621}. Council Decision 82/72/EEC of December3 (1981 concerning the conclusion of the Convention on the conservation of European wildlife and natural habitats (Bern Convention). Convention on Biological Diversity (CBD) signed by the Community and all the Member States at the United Nations Conference on Environment and Development in Rio de Janeiro from 3 to 14 June 1992
Soil protection	Communication from the Commission to the Council, the European Parliament, the European Economic and Social Committee and the Committee of the Regions - Thematic Strategy for Soil Protection [SEC(2006)620] [SEC(2006)1165] /* COM/2006/0231 final */ Proposal for a Directive of the European Parliament and of the Council establishing a framework for the protection of soil and amending Directive 2004/35/EC /* COM/2006/0232 final - COD 2006/0086 */ Commission staff working document - Accompanying document to the Communication from the Commission to the Council, the European Parliament, the European Economic and Social Committee and the Committee of the Regions - Thematic Strategy for Soil Protection - Summary of the impact assessment {COM(2006)231 final} {SEC(2006)620} /* SEC/2006/1165 */ Commission staff working document - Document accompanying the Communication from the Commission to the Council, The European Parliament, the European Economic and Social Committee and the Committee of the Regions - Thematic Strategy for Soil Protection - Impact assessment of the thematic strategy on soil protection {COM(2006)231 final} {SEC(2006)1165} /* SEC/2006/0620 */ Directive 2004/35/CE of the European Parliament and of the Council of April 21, 2004 on environmental liability with regard to the prevention and remedying of environmental damage. Council Directive 85/337/EEC of June 27 (1985 on the assessment of the effects of certain public and private projects on the environment and subsequent amendments and integra tions.
Civil protection	Omitted.
Climate change	Commission of the European Communisties - Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the regions. Analysis of options to move beyond 20% greenhouse gas emission reductions and assessing the risk of carbon leakage (2010) Background information and analysis, part I and II Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions - 20 20 by 2020 - Europe's climate change opportunity {COM(2008) 13 final} {COM(2008) 16 final} {COM(2008) 17 final} {COM(2008) 18 final} {COM(2008) 19 final} /* COM/2008/0030 final */ Directive 2009/29/EC of the European Parliament and of the Council of 23 April 2009 amending Directive 2003/87/EC so as to improve and extend the greenhouse gas emission allowance trading scheme of the Community Text with EEA relevance Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC Text with EEA relevance Directive 2003/87/EC of the European Parliament and of the Council of October 13, 2003 establishing a scheme for greenhouse gas emission allowance trading within the Community and amending Council Directive 96/61/EC. Directive 2004/101/EC of the European Parliament and of the Council of October 227, 004 amending Directive 2003/87/EC establishing a scheme for greenhouse gas emission allowance trading within the Community, in respect of the Kyoto Protocol's project mechanisms. Commission Regulation (EC) No 2216/2004 of December 21, 2004 for a standardized and secured system of registries pursuant to Directive 2003/87/EC of the European Parliament and of the Council and Decision No 280/2004/EC of the European Parliament and of the

	Council. 2006/780/EC: Commission Decision of November 13, 2006 on avoiding double counting of greenhouse gas emission reductions under the Community emissions trading scheme for project activities under the Kyoto Protocol pursuant to Directive 2003/87/EC of the European Parliament and of the Council. Commission Communication of February 9, 2005 "Winning the battle against global climate change. Communication from the Commission, of January 10, 2007, entitled: "Limiting Global Climate Change to 2 degrees Celsius - The way ahead for 2020 and beyond. Communication from the Commission of March 8, 2000 on EU policies and measures to reduce greenhouse gas emissions: towards a European Climate Change Program (ECCP). 2002/358/EC: Council Decision of April 25, 2002 concerning the approval, on behalf of the European Community, of the Kyoto Protocol to the United Nations Framework Convention on Climate Change and the joint fulfillment of commitments thereunder

The average brick maker is directly only confronted with the IPPC directive 96/61/EC concerning integrated pollution prevention and control, twice amended to include emissions trading and public participation. The aim of the IPPC directive is to minimize the environmental impact of industrial production processes, both new and existing. The IPPC directive and authorization process is based on BAT best available techniques agreed between industry and the legislator. The activity of writing up the European BAT documents has been taken up by the European IPP Bureau. In many member states, due to the diversity of the brick produced, additional national BAT documents have been issued.

Appendix VI

A South Tyrolean Case Study: Mattoni Gasser Ziegel GmbH S.r.l.

Published papers (selection)

Patents (selection)

Esperienze aziendali nel recupero dei rifiuti: condizioni contrattuali e procedure interne di controllo e gestione

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Il recupero di rifiuti nell'industria dei laterizi tende pressoché a bilanciare i rifiuti prodotti dallo stesso settore. La scelta del rifiuto, le condizioni contrattuali di fornitura e la definizione di procedure interne di controllo e gestione risultano fasi essenziali per gestire l'attività di recupero senza pregiudicare il processo produttivo e le prestazioni del prodotto.

IL RECUPERO DEI RIFIUTI NELL'INDUSTRIA DEI LATERIZI

La normativa ambientale

La normativa vigente - D.Lgs. 22/97 e D.M. 05/02/98 - individua, tra le attività di recupero di diversi rifiuti speciali "non pericolosi", l'impiego nell'industria dei laterizi. La stessa normativa prescrive solo per alcuni rifiuti una caratterizzazione chimica, con indicazione di limiti sulle concentrazioni di alcuni componenti (in particolare gli ossidi metallici), mentre subordina le attività di recupero ambientale e di rilevati e sottofondi stradali (attività che prevedono la disposizione del rifiuto sul suolo) all'esecuzione del test di cessione, funzionale, quindi, alla valutazione del potenziale rilascio di inquinanti per azione delle piogge acide.

Dati di settore per il recupero dei rifiuti

Il settore dei laterizi è particolarmente attento alle problematiche ambientali, tant'è che il recupero dei rifiuti non pericolosi tende a bilanciare la produzione dei rifiuti dovuti all'attività industriale.

I rifiuti recuperati sono principalmente i fanghi provenienti dalle cartiere, dall'industria ceramica e dagli impianti di trattamento acque - più dell'80% - nonché le terre di fonderia e le ceneri di carbone.

Perché non è sufficiente rispettare la norma?

I laterizi sono da sempre considerati un prodotto "ecologico" e "naturale"; lo stesso processo produttivo è tale da consentire il recupero dei rifiuti in sostituzione di risorse naturali.

È evidente, però, che l'impiego dei rifiuti nell'impasto deve essere accuratamente valutato e controllato dal produttore, affinché sia ottimizzato il processo produttivo, in termini di condizioni operative e di emissioni, e siano garantite le prestazioni tecniche ed ambientali del prodotto.

La caratterizzazione chimica dei rifiuti utilizzati nell'impasto si rende oltremodo necessaria, perché la formulazione dello stesso incide sia sulle condizioni di esercizio degli impianti e sulle emissioni che ne derivano, sia sulle proprietà del prodotto:

- *in termini di processo*, risulta essenziale la caratterizzazione degli ossidi, la cui presenza comporta variazioni del profilo termico di cottura, e la caratterizzazione del cromo e del cloro, per gli effetti corrosivi sulle parti metalliche dell'essiccatoio e del forno, oltre che per la produzione di emissioni inquinanti;
- *in termini di prodotto*, risulta importante la caratterizzazione dei carbonati, che incrementano l'efflorescenza dei laterizi, e la valutazione della granulometria e della capacità di assorbimento d'acqua dell'impasto, con effetti sulle caratteristiche fisiche dei laterizi.

Standard di riferimento

Essenziale per l'impiego dei rifiuti nell'impasto risulta la definizione di uno standard di riferimento (c.d. "bianco"), costituito dall'analisi delle materie prime impiegate e dalla valutazione del comportamento chimico-fisico dei prodotti intermedi e finali. La definizione di tale standard consente all'azienda la valutazione ed il confronto delle caratteristiche prestazionali ed ambientali del prodotto, a seguito dell'impiego dei rifiuti.

Criteri di scelta del rifiuto

Il criterio per la scelta di un rifiuto da recuperare nell'impasto è che esso non comporti effetti negativi intollerabili sulla specifica produzione.

L'importanza di uno standard di riferimento consiste, proprio, nella possibilità di valutare le variazioni sul processo e sulle prestazioni dello specifico prodotto, dovute all'aggiunta del rifiuto all'impasto. Tali variazioni assumono carattere positivo o negativo in funzione del prodotto da ottenere; ad esempio, se si desidera aumentare le proprietà di isolamento termico, l'aggiunta di fanghi di cartiera all'impasto migliorerà tale caratteristica, comportando un incremento della porosità, a scapito, però, di una diminuzione della resistenza alla compressione.

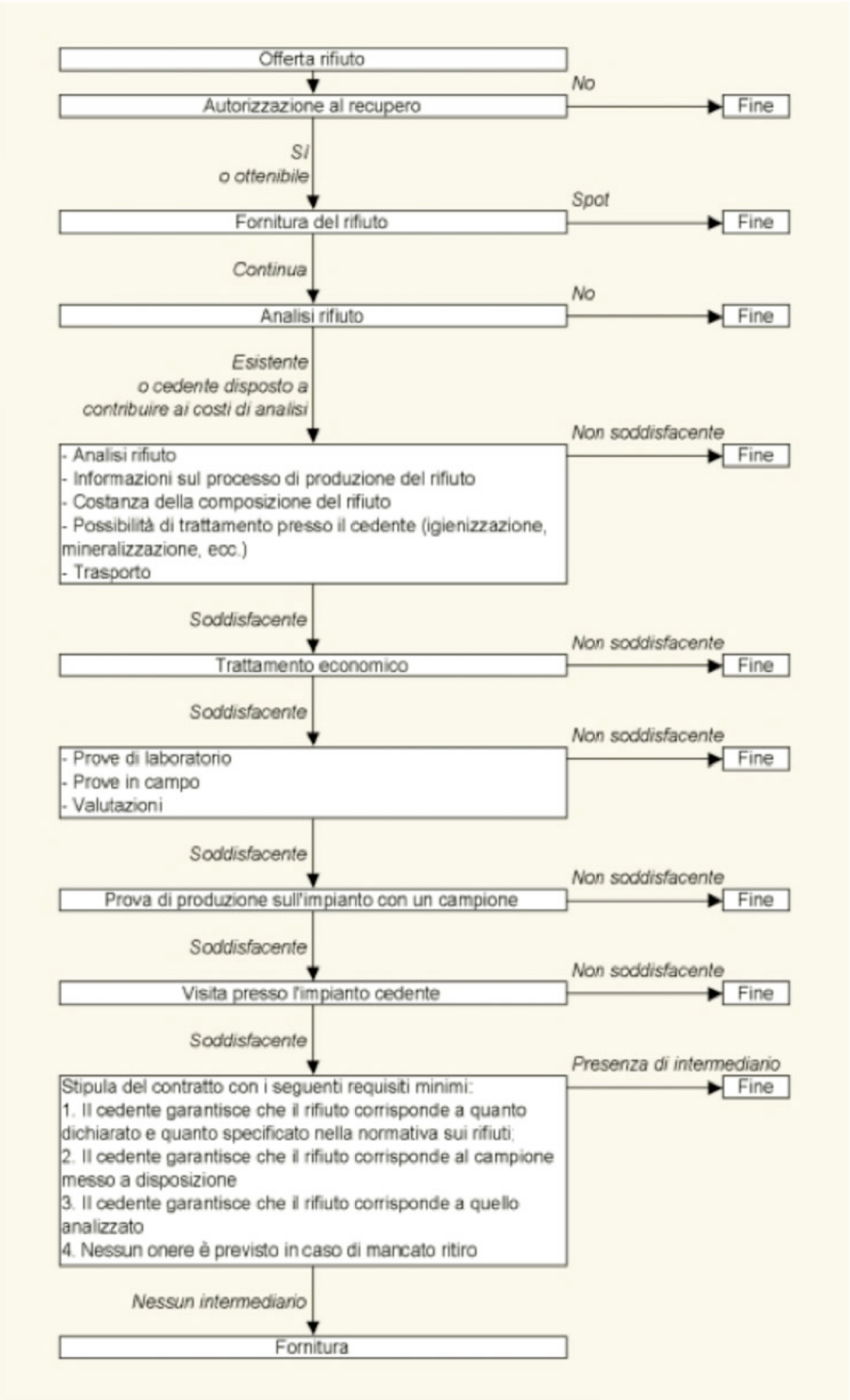


Fig. 1 - Criteri per la stipula di un contratto di fornitura di rifiuti ai fini del recupero.

L'ESPERIENZA DELLA FORNACE GASSER DI BRESSANONE

Molte fornaci, sulla base delle proprie esperienze, hanno definito delle procedure interne per stabilire l'opportunità e la convenienza economica ed ambientale di utilizzare nei propri impasti rifiuti di vario genere. Nel seguito, si riportano le procedure che la fornace Gasser di Bressanone, comunemente, adotta per attivare un contratto di fornitura di rifiuti da recuperare. Tali procedure riguardano sia le condizioni generali per la stipula del contratto di fornitura, sia le fasi operative di accettazione del rifiuto e di verifica e controllo dei materiali e dei prodotti.

CONTRATTO DI FORNITURA

Nell'attività di recupero dei rifiuti, esiste una diversità di interessi tra le parti, laddove il fornitore considera il rifiuto come qualcosa di cui disfarsi in tempi brevi e a bassi costi, mentre chi recupera considera il rifiuto come materia prima.

Condizioni essenziali per la stipula del contratto di acquisto del rifiuto si basano sulla conoscenza approfondita dello stesso e degli effetti che il suo impiego nell'impasto può apportare al processo ed al prodotto; ma opportune garanzie devono derivare anche dall'interlocutore che partecipa all'accordo, per esaminare la serietà ed affidabilità del cedente. In tal senso, è consigliabile diffidare degli intermediatori e trattare direttamente con il produttore del rifiuto, al quale è conveniente richiedere le opportune referenze: informazioni commerciali, sulle autorizzazioni degli impianti, sulle certificazioni di qualità e di processo, ecc.

Spesso, una visita allo stabilimento produttore del rifiuto può rendersi necessaria per acquisire le giuste indicazioni sulla serietà dell'interlocutore.

Ai fini del contratto, è poi indispensabile definire il compenso economico, i tempi e i modi di consegna, la responsabilità del trasportatore, la possibilità di interrompere la fornitura da parte del ricevente ed i relativi oneri (fig. 1).

PROCEDURA DI ACCETTAZIONE ED IMPIEGO DEL RIFIUTO

Prima della stipula del contratto di fornitura, un campione del rifiuto deve essere rigorosamente analizzato e provato sullo specifico impianto produttivo. Di tale campione è opportuno conservare una congrua quantità per determinare, in caso di controversie, le rispettive responsabilità.

Tale valutazione viene quindi effettuata una tantum, mentre, per la singola fornitura, è conveniente attenersi ad una specifica procedura di accettazione del rifiuto e di gestione e controllo della produzione, tale da rendere rintracciabile ed inconfutabile l'eventuale inosservanza dei requisiti del rifiuto (fig. 2).

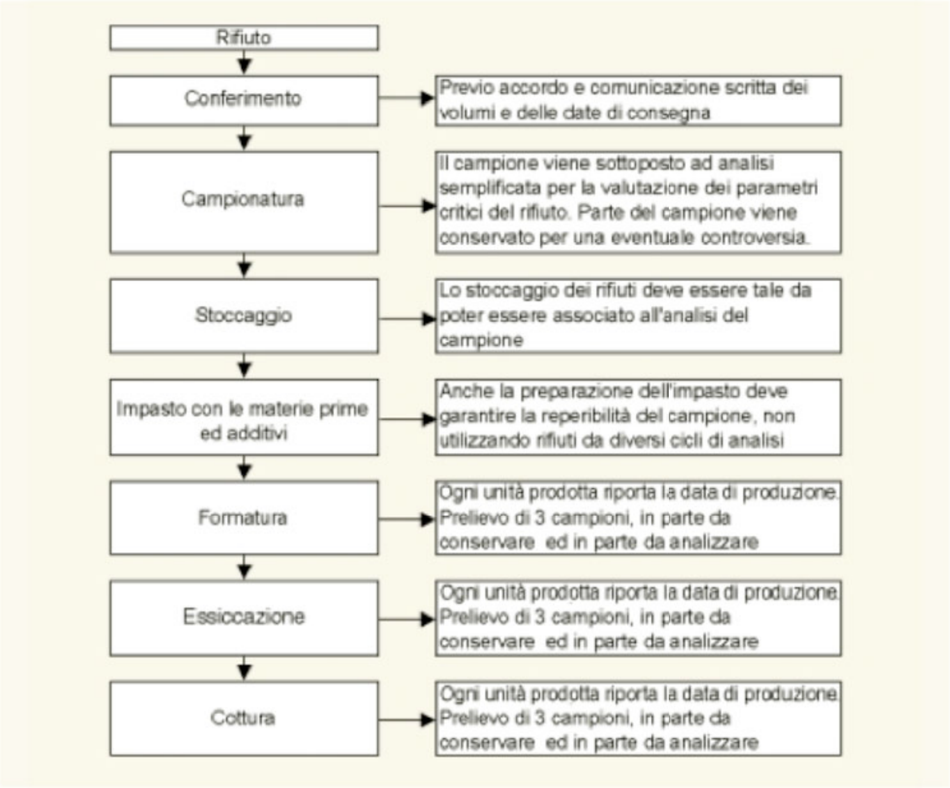


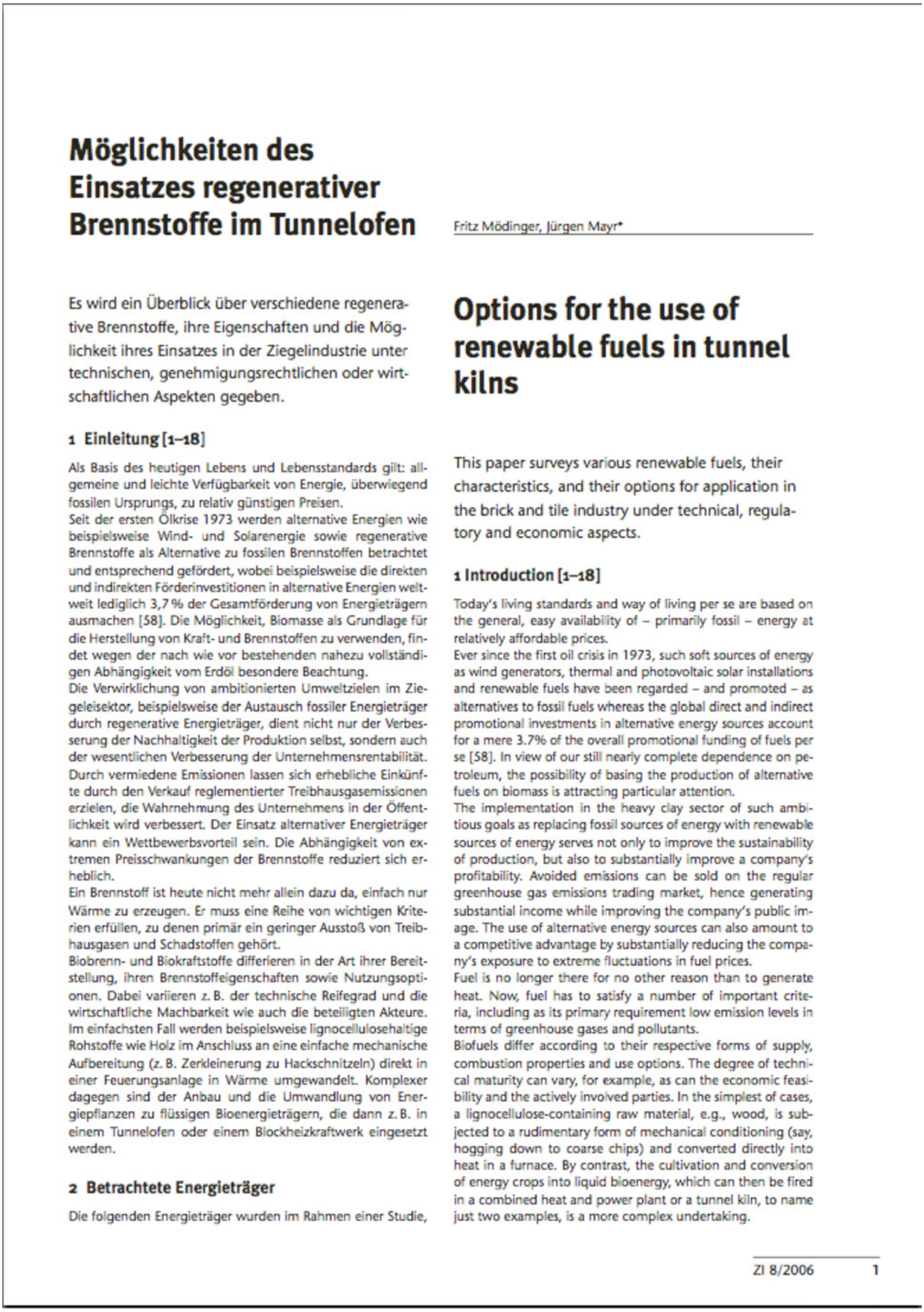
Fig. 2 - Procedura di accettazione del rifiuto e di gestione e controllo della produzione.

VERIFICHE E CONTROLLI SUI MATERIALI E SUI PRODOTTI

La continua verifica e controllo delle caratteristiche dei materiali e dei prodotti si rendono ancor più necessari ed approfonditi in caso di recupero di rifiuti. Affinché sia controllato il processo e siano garantite le prestazioni del prodotto, frequenti devono essere le caratterizzazioni delle materie in ingresso (materie prime e rifiuti), del prodotto secco e del prodotto finale e le indicazioni riportate in tabella I possono costituire un utile punto di riferimento.

Tab. I - Programma di caratterizzazione delle materie prime, dei rifiuti e del prodotto secco e cotto.

Analisi/Frequenza	Materia prima	Rifiuti	Prodotto secco	Prodotto cotto
Analisi chimica elementare	annuale (anche sul fronte di cava)	trimestrale (su ogni fornitura saltuaria)	Mensile	Mensile
Calcolo delle proprietà ceramiche	ad ogni analisi		a seguito di variazioni dell'impasto	
Prove di cottura	annuale (anche sul fronte di cava)		a seguito di variazioni dell'impasto	
Test di cessione		trimestrale		mensile
Plasticità	mensile		giornaliera	
Contenuto d'acqua	più volte al giorno	più volte al giorno	più volte al giorno	
Carbonati	annuale (anche sul fronte di cava)			mensile
Granulometria	annuale (anche sul fronte di cava)			
Perdita di peso su secco	settimanale		giornaliera (almeno 15 campioni)	
Ritiro su secco	settimanale		giornaliera (almeno 15 campioni)	
Ritiro per cottura	trimestrale (anche sul fronte di cava)			giornaliera (almeno 15 campioni)
Flessione su listello	trimestrale (anche sul fronte di cava)		mensile	
Assorbimento d'acqua	trimestrale (anche sul fronte di cava)			giornaliera (15 campioni)
Inclusioni calcaree	trimestrale (anche sul fronte di cava)			settimanale
Resistenza al gelo	trimestrale (anche sul fronte di cava)			mensile (15 campioni)
Porosità	trimestrale (anche sul fronte di cava)			settimanale
Efflorescenza	trimestrale (anche sul fronte di cava)			giornaliera (su 3 campioni)
Resistenza alla compressione	trimestrale (anche sul fronte di cava)			mensile (15 campioni)



Möglichkeiten des Einsatzes regenerativer Brennstoffe im Tunnelofen

Fritz Mödinger, Jürgen Mayr*

Es wird ein Überblick über verschiedene regenerative Brennstoffe, ihre Eigenschaften und die Möglichkeit ihres Einsatzes in der Ziegelindustrie unter technischen, genehmigungsrechtlichen oder wirtschaftlichen Aspekten gegeben.

1 Einleitung [1–18]

Als Basis des heutigen Lebens und Lebensstandards gilt: allgemeine und leichte Verfügbarkeit von Energie, überwiegend fossilen Ursprungs, zu relativ günstigen Preisen.

Seit der ersten Ölkrise 1973 werden alternative Energien wie beispielsweise Wind- und Solarenergie sowie regenerative Brennstoffe als Alternative zu fossilen Brennstoffen betrachtet und entsprechend gefördert, wobei beispielsweise die direkten und indirekten Förderinvestitionen in alternative Energien weltweit lediglich 3,7 % der Gesamtförderung von Energieträgern ausmachen [58]. Die Möglichkeit, Biomasse als Grundlage für die Herstellung von Kraft- und Brennstoffen zu verwenden, findet wegen der nach wie vor bestehenden nahezu vollständigen Abhängigkeit vom Erdöl besondere Beachtung.

Die Verwirklichung von ambitionierten Umweltzielen im Ziegeleisektor, beispielsweise der Austausch fossiler Energieträger durch regenerative Energieträger, dient nicht nur der Verbesserung der Nachhaltigkeit der Produktion selbst, sondern auch der wesentlichen Verbesserung der Unternehmensrentabilität. Durch vermiedene Emissionen lassen sich erhebliche Einkünfte durch den Verkauf reglementierter Treibhausgasemissionen erzielen, die Wahrnehmung des Unternehmens in der Öffentlichkeit wird verbessert. Der Einsatz alternativer Energieträger kann ein Wettbewerbsvorteil sein. Die Abhängigkeit von extremen Preisschwankungen der Brennstoffe reduziert sich erheblich.

Ein Brennstoff ist heute nicht mehr allein dazu da, einfach nur Wärme zu erzeugen. Er muss eine Reihe von wichtigen Kriterien erfüllen, zu denen primär ein geringer Ausstoß von Treibhausgasen und Schadstoffen gehört.

Biobrenn- und Biokraftstoffe differieren in der Art ihrer Bereitstellung, ihren Brennstoffeigenschaften sowie Nutzungsoptionen. Dabei variieren z. B. der technische Reifegrad und die wirtschaftliche Machbarkeit wie auch die beteiligten Akteure. Im einfachsten Fall werden beispielsweise lignocellulosehaltige Rohstoffe wie Holz im Anschluss an eine einfache mechanische Aufbereitung (z. B. Zerkleinerung zu Hackschnitzeln) direkt in einer Feuerungsanlage in Wärme umgewandelt. Komplexer dagegen sind der Anbau und die Umwandlung von Energiepflanzen zu flüssigen Bioenergieträgern, die dann z. B. in einem Tunnelofen oder einem Blockheizkraftwerk eingesetzt werden.

2 Betrachtete Energieträger

Die folgenden Energieträger wurden im Rahmen einer Studie,

Options for the use of renewable fuels in tunnel kilns

This paper surveys various renewable fuels, their characteristics, and their options for application in the brick and tile industry under technical, regulatory and economic aspects.

1 Introduction [1–18]

Today's living standards and way of living per se are based on the general, easy availability of – primarily fossil – energy at relatively affordable prices.

Ever since the first oil crisis in 1973, such soft sources of energy as wind generators, thermal and photovoltaic solar installations and renewable fuels have been regarded – and promoted – as alternatives to fossil fuels whereas the global direct and indirect promotional investments in alternative energy sources account for a mere 3.7% of the overall promotional funding of fuels per se [58]. In view of our still nearly complete dependence on petroleum, the possibility of basing the production of alternative fuels on biomass is attracting particular attention.

The implementation in the heavy clay sector of such ambitious goals as replacing fossil sources of energy with renewable sources of energy serves not only to improve the sustainability of production, but also to substantially improve a company's profitability. Avoided emissions can be sold on the regular greenhouse gas emissions trading market, hence generating substantial income while improving the company's public image. The use of alternative energy sources can also amount to a competitive advantage by substantially reducing the company's exposure to extreme fluctuations in fuel prices.

Fuel is no longer there for no other reason than to generate heat. Now, fuel has to satisfy a number of important criteria, including as its primary requirement low emission levels in terms of greenhouse gases and pollutants.

Biofuels differ according to their respective forms of supply, combustion properties and use options. The degree of technical maturity can vary, for example, as can the economic feasibility and the actively involved parties. In the simplest of cases, a lignocellulose-containing raw material, e.g., wood, is subjected to a rudimentary form of mechanical conditioning (say, hogging down to coarse chips) and converted directly into heat in a furnace. By contrast, the cultivation and conversion of energy crops into liquid bioenergy, which can then be fired in a combined heat and power plant or a tunnel kiln, to name just two examples, is a more complex undertaking.

die 2002 von der Ziegelei Gasser ausgeführt wurde, einer Betrachtung unterzogen. In Tabelle 1 sind auch die nachfolgend im Detail erläuterten Ergebnisse in Bezug auf die **technische Machbarkeit** in der Ziegelindustrie zusammengefasst:

- ▶ NG: nicht geeignet
- ▶ BG: bedingt geeignet
- ▶ GG: geeignet

Die Ergebnisse in Bezug auf eine **wirtschaftliche Machbarkeit**, ebenfalls in Tabelle 1 angegeben, sind:

- ▶ – = nicht machbar
- ▶ + = machbar

Es zeigt sich, dass gewisse Stoffe vom wirtschaftlichen Standpunkt her interessant wären, jedoch die technische Machbarkeit, so wie nachfolgend erläutert, nicht gegeben ist.

3 Feste Brennstoffe [19–29]

Der Einsatz von festen Brennstoffen setzt einen hohen technischen Aufwand voraus. Ein Problem stellen ferner die Verbrennungsrückstände (Aschen) dar, die sich auf der Ware absetzen. Die energetische Nutzung von festen Brennstoffen wird auch in [30, 31] behandelt.

3.1 Holz

Holz war lange Zeit nicht nur das wichtigste Baumaterial, sondern auch der einzige Energieträger. Mit der einsetzenden Industrialisierung verdrängten fossile Energieträger das Holz in zunehmendem Maße. Die Eigenschaften des Brennstoffes Holz werden im Wesentlichen von seinem besonderen Aufbau und

2 Subject energy sources

The following energy sources were investigated within the scope of a study performed by Ziegelei Gasser in 2002. The findings with regard to **technical feasibility** in the heavy clay industry are detailed below and summarized in Table 1:

- ▶ NS: not suitable
- ▶ CS: conditionally suitable
- ▶ FS: fully suitable

With regard to **economic feasibility**, Table 1 lists the results as either:

- ▶ – = unfeasible
- ▶ + = feasible

The findings show that some kinds of material are of potential interest in the economic sense but lacking in technical feasibility, as explained below.

3 Solid fuels [19–29]

The use of solid fuels involves major plant and equipment requirements, and the combustion residue (ashes) that settles on the products poses a problem. The use of solid fuel as a source of energy is also discussed in [30, 31].

3.1 Wood

For a long time wood was not only the building material of choice, but also the sole source of energy. With the onset of industrialization, however, fossil fuels gradually and largely replaced wood. The characteristics of wood as a fuel are ex-

Tabelle 1: Übersicht der betrachteten Energieträger
Table 1: Summary of subject energy sources

Bezeichnung Designation	**Holz und Halmgüter Wood & stem plants**	**Energiepflanzen (Stroh/Heu/Getreide = Mittelwert) Energy plants**	**Tiermehl Meat + bone meal**	**Klärschlamm Sewage sludge**	**Biogas**	**Pflanzenöl (Rapsöl/Sojaöl = Mittelwert) Vegetable oil**	**Tierfett (Mittelwerte) Animal fat (mean values)**	**Schweröl (Mittelwerte) Heavy oil (mean values)**
Heizwert HU [MJ/kg] Calorific value gross/net [MJ/kg]	14.1–18.8	16	22	8–11.5	24.9–36	36.65	36.3	40.3
Aschegehalt [%] Ashe content [%]	0.5–23.00	6.8	22.0–31.0	–	n.n.	0.005	< 0.11	0.1
Wasserstoff/Hydrogen	5.07–7.7	6	7.7	3–4	0–1	12	11.32	10.6–11.0
Stickstoff/Nitrogen	5.8–10.6	0.89	5.8	1.9–6	2	663	0.32	0.4
S Fluoride [mg/kg] S Fluoride [mg/kg]	30			100–1 000	*		< 1000	
S Chlor/Chlorine	0.0076	0.04		1.9–6	*	11	0.07	10–500
Gesamtschwefel [%] Total sulphur [%]	0.0382	0.33–0.62	0.5	0.5–1.3	0–1	5	0.22	2.8–3.5
Quecksilber [mg/kg] Mercury [mg/kg]	0.225	< 0.05	0.18	2.3	n.n		< 0.10	n.n.
Kohlenstoff [%] Carbon [%]	49	46	37.2	22–31		0.4	73.32	84–84.9
Arsen/Arsenic [mg/kg]	1.4	< 0.8	0.3	5–50	n.n.	–	< 20.0	10–500
Blei/Lead [mg/kg] (trocken)	5	< 5.0	4.25	200–390	n.n.	0.1	< 20.0	153
Cadmium/Cadmium	0.25	< 0.5	0.43	3.6–4.3	n.n.	–	< 2	
Chrom/Chrome	4	< 5.0	8.31	64–72	n.n.	–	< 3	0.01
Kupfer/Copper	12.5	10		322	n.n.	0.06	< 3	10–500
Nickel/Nickel	1.7	1.02875		10–50	n.n.	–	< 3	80

n.n. Nicht nachweisbar
* < 1%

seiner chemischen Zusammensetzung bestimmt. Holz ist keine homogene Substanz, sondern besteht aus einer Vielzahl einzelner Zellen. Das, was wir als Holz bezeichnen, ist im Wesentlichen die Zellwandsubstanz. Diese besteht zu etwa 50 % aus Cellulose, aus Lignin und Holzpolyosen. Außerdem enthält Holz geringe Mengen an so genannten Extraktstoffen (Harze, Fette, Stärke, Gerbstoffe u. a.) sowie Mineralstoffe. Die Hauptbestandteile des Holzes sind Kohlenstoff, Sauerstoff, Wasserstoff. Die Spurenelemente im Holz nehmen in etwa 10 g/kg ein. Der Schwefel wird bei der ordnungsgemäßen Verbrennung von Holz zum großen Teil in die Asche eingebunden. Schwefeldioxid wird deshalb nur in geringen Mengen emittiert. Der Holzstickstoff führt hingegen zur Bildung von Stickoxiden, die als Schadstoffe an die Umwelt abgegeben werden.

Für die Verbrennung ist von Bedeutung, dass der Hauptteil der Holzsubstanz bei der Erwärmung in flüchtige Bestandteile aufgespalten wird. Rund 82 % der Holzmasse werden vor der Oxidation zu Gasen umgewandelt, nur 18 % verbrennen als Holzkohle und knapp 1 % bleibt als Asche zurück. Es verbrennen also nicht in erster Linie das Holz selbst, sondern die bei der Pyrolyse freigesetzten Gase. Holz ist deshalb ein langflammiger Brennstoff.

Für eine emissionsarme Energienutzung von naturbelassenem Holz gilt es, eine vollständige Verbrennung der Gase zu erzielen, um so die Emissionen an Kohlenmonoxid, Kohlenwasserstoffen und Ruß zu minimieren. Als Grundvoraussetzung für eine gute Verbrennung müssen die brennbaren Gase genügend Zeit haben, um bei hohen Temperaturen vollständig zu verbrennen. Sowohl beim Einsatz von zu feuchtem Holz als auch bei mangelnder Luftzuführung kommt es zu erheblichen Umweltbelastungen durch starke Rauch- und Rußbildung. Gute Indikatoren für die Qualität der Verbrennung sind Farbe und Beschaffenheit der Asche. Bei einer sauberen Verbrennung entsteht eine feine weiße Asche. Eine dunkle Färbung deutet auf Holzkohlereste hin, die – bedingt durch einen unvollständigen Ausbrand – in der Asche zu finden sind. Bei der Verbrennung von Holz werden Aerosole mit dem Rauchgas freigesetzt. Aerosole sind in der Luft verteilte, feste oder flüssige Partikel und Partikelansammlungen im Größenbereich zwischen 0,001 und 100 µm. Bei unvollständiger Verbrennung entstehen Aerosole wie Ruß oder unverbrannte schwerflüchtige organische Kohlenstoffverbindungen. Bei vollständiger Verbrennung entstehen Aerosole, wie z. B. anorganische Mineralstoffe. Die Bildung von Aerosolen aus vollständiger Verbrennung kann dagegen nicht primär beeinflusst werden, sondern diese müssen sekundär durch filternde Abscheider oder Nachverbrennung vermindert werden. Durch unvollständige Verbrennung des Holzes kommt es vor allem zur Bildung von Kohlenstoffmonoxid und zahlreichen organischen Verbindungen, wie beispielsweise Dioxinen und Furanen, die Zwischenprodukte des Verbrennungsvorgangs darstellen. Ein weiteres Problem stellen eventuell eingetragene Schadstoffe, wie etwa Fungizide usw., dar. Biogene Festbrennstoffe enthalten in geringen Mengen chemisch gebundenen Stickstoff. Dieser Stickstoff hat in der Regel auch eine entsprechende NO_x-Emission zur Folge. Bei der Verbrennung von Holz sind auf Grund der sehr geringen Stickstoffgehalte die niedrigsten NO_x-Emissionen im Vergleich zu anderen Biomassefraktionen (z. B. Stroh, Getreidepflanzen) zu erwarten und eine Einhaltung der Grenzwerte ist möglich. Schwefel- und Chlorverbindungen spielen bei holzartigen Brennstoffen eine untergeordnete Rolle, da deren Gehalt sehr gering ist und Emissionen dieser Schadstoffe überwiegend aus brennstoffgebundenen Quellen herrühren. Bei der Verbrennung von Holz bleiben die im Brennstoff enthaltenen Mineral-

tensively determined by its particular structure and chemical composition. Wood is not a homogeneous material, but instead consists of myriad individual cells. What we call wood is actually the cell wall substance, roughly half of which consists of cellulose, lignin and wood polyoses. Wood also contains small amounts of so-called extractive materials (resins, fats, starch, tannin, etc.) and mineral substances. The main constituents of wood are carbon, oxygen and hydrogen. Trace elements account for approx. 10 g/kg. When wood is burnt properly, most of its sulphur content will remain behind in the ash. Consequently, only little sulphur dioxide will be emitted. Conversely, wood nitrogen leads to the formation of nitrogen oxides, which, when emitted to the environment, act as pollutants.

For good combustion, it is important that most of the wood substance break down into its volatile constituents when heated. Head-induced oxidation transforms roughly 82% of the wood mass to gas, with only 18% actually burning off as wood coal and barely 1% remaining behind as ash. Hence, what actually burns is not so much the wood itself, but the gases released by pyrolysis. Hence, wood is a long-flame fuel.

Low-emission exploitation of energy from natural wood therefore requires complete combustion of the gases in order to minimize the release of carbon monoxide, hydrocarbons and soot. The basic prerequisite for good combustion is that the combustible gases have enough time to burn completely at high temperatures. If the wood is too moist, or if the air supply is deficient, the resultant smoke and soot will constitute a substantial negative environmental impact. The colour and general appearance of the ash are good indicators of the quality of combustion. Good, clean combustion produces fine, white ashes. Dark ashes indicate the presence of residual charcoal due to incomplete combustion. Burning wood releases aerosols with the combustion gases. Aerosols are defined as disperse solid or liquid particles and particle agglomerations measuring between 0.001 and 100 µm in size. Incomplete combustion produces aerosols like soot or unburnt, heavy carbon compounds, while complete combustion produces such aerosols as inorganic mineral matter. However, the formation of aerosols from complete combustion cannot be primarily influenced, but only via such secondary means as particulate removal equipment or aftercombustion. The main problem with incomplete combustion of wood is that it generates carbon monoxide and numerous organic compounds like dioxins and furans as intermediate products of combustion. Potential contamination in the form of fungicides, etc. is also problematic. Biogenic solid fuels contain small amounts of chemically bonded nitrogen that usually emerge as corresponding NO_x emissions. On the other hand, since wood contains very little nitrogen, the resultant NO_x emissions are very minor compared to those of other biomass fractions (e.g., straw, cereal plants), and compliance with the limit values is possible. Sulphur and chlorine compounds play only a minor role in woody fuels, because wood contains very little of both, and most such emissions stem from fuel-bound sources. The minerals contained in wood remain behind in the ash following combustion. Depending on the quality of combustion, the ash will contain a greater or lesser quantity of residual combustible material (charcoal).

3.2 Stem plants

The same criteria as those stated above for wood remain valid for the use of straw and other stem plants as fuel, the main difference – and additional limiting factor – being that they are stoffe als Asche zurück. Je nach Güte des Ausbrandes ist in der Asche noch ein Anteil an brennbaren Bestandteilen enthalten (Holzkohle).

3.2 Halmgut

Für Halmgut (Stroh) können dieselben Kriterien dienen, die auch für Holz als Brennstoff gelten. Eine weitere Einschränkung gegenüber Holz ist die sicher höhere Belastung mit chemischen Stoffen, die in der Landwirtschaft Einsatz finden.

3.3 Energiepflanzen

Bei Energiepflanzen darf man von einem Heizöläquivalent von knapp 3 000 l und über 6 000 l je Hektar Anbaufläche ausgehen. Die Energiebilanzen erscheinen auf den ersten Blick positiv. In Mischung mit Steinkohle nehmen NO_x- und SO_2-Emissionen mit zunehmendem Biomasseanteil ab, die CO_x-Emissionen dagegen zu.

Für den Anbau als Energiepflanzen eignen sich Kulturen nur bei entsprechend hohen Ganzpflanzenerträgen. Raps und Sonnenblumen sind wegen der hohen Kornverluste hierfür ungeeignet. Besser geeignet sind beispielsweise, vor allem in subtropischen Gebieten und Ländern der Sahel-Zone, Jatropha und Palmen. Die organischen Anbaureste können direkt in einer Biogasanlage verarbeitet werden.

Getreide und Halmgut eignen sich, um trockenes (= lagerfähiges) Gut zu erhalten. Bei Mais erhält man auch bei später Ernte im Winter ohne Trocknung länger lagerfähiges Gut. Beim unterstellten Anbau der Energiepflanzen auf Stilllegungsflächen sind die landwirtschaftlichen Biomassen gegenüber Heizöl nur teilweise wirtschaftlich konkurrenzfähig. Die Verbrennung bzw. Mitverbrennung von Biomassen in einer Kohlestaubverbrennungsanlage sind technisch und auch in Bezug auf Emissionen möglich. Die positive Energiebilanz macht die Verwendung fester Biomasse als Energieträger interessant. Die Wirtschaftlichkeit der Biomassen wird von der Entwicklung des Preises der fossilen Energieträger abhängig sein.

3.4 Tiermehl

Tiermehl kann zu Methanol aufbereitet oder als direkter Brennstoff in Großfeuerungsanlagen eingesetzt werden.

Heute werden Tierabfälle gesammelt und im geschlossenen Lkw zur nächsten Tierkörperbeseitigungsanstalt transportiert. Dort landen diese in so genannten Brechern und werden zu Brei geschreddert, der 20 Minuten unter einem Druck von 3 bar auf 133 °C erhitzt wird. Anschließend wird das Ganze getrocknet, zwei Drittel der Feuchtmasse verdampfen. Die Trockenmasse wird gepresst, wobei sich Fett und Eiweiß trennen. Als Pulver, in Blöcken oder in flüssiger Form kehrt das Produkt in den Wirtschaftskreislauf zurück.

Tiermehl hat einen Heizwert von 16 000 bis 22 000 kJ/kg. Das entspricht annähernd dem Heizwert von Braunkohle (ca. 23 500 kJ/kg). Die Schwermetallgehalte des Tiermehls sind sehr gering. Sie liegen weit unterhalb der Schwermetallgehalte einer üblichen Kohle.

3.5. Getrockneter Klärschlamm

Getrockneter Klärschlamm könnte ebenfalls als Brennstoff in Betracht kommen. Er wird in Klärschlammtrocknungsanlagen mit dem Ziel der Volumenreduzierung der Abfallströme erzeugt.

4 Gasförmige Brennstoffe [32–56]

Biogas ist, wie auch Deponie- und Klärgas, ein Stoffwechselprodukt von Methanbakterien. Die Biogasbildung ist dabei ein in

sure to contain more chemical substances of the kinds used in agriculture.

3.3 Energy plants

Energy plants can be postulated as yielding a fuel oil equivalent of nearly 3 000 to 6 000 litres per hectare. At first glance, their energy balances appear positive. When mixed with hard coal, the blended fuel's NO_x and SO_2 emissions decrease in inverse proportion to the biomass fraction, but the CO_x emissions increase.

Only cultivars offering appropriately high whole-plant yields are suitable for cultivation as energy plants. Rape/colza and sunflowers are unsuitable due to their high grain-loss rates. Among those better suited for the purpose, particularly in subtropical climates and Sahel-Zone countries are Jatropha and Palms, the organic crops residues of which can be fed directly into biogas plants.

Cereal and stem plants make good dry (= storable) fuel products, and maize/corn stores well in winter without drying if it is harvested late. Postulating the cultivation of energy crops on set-aside land, the resultant agricultural biomass yields are not fully competitive in relation to fuel oil. The burning or co-burning of biomass in a coal dust combustion plant is feasible, both in the technical sense and with regard to emissions. The positive energy balance of solid biomass makes it an attractive source of energy. The economic efficiency of biomass remains dependent on the rise and fall of fossil-fuel prices.

3.4 Meat and bone meal

Meat and bone meal (also known as tankage) can be processed to obtain methanol but can also serve directly as fuel in large combustion systems.

In some places, animal waste is collected and hauled in covered trucks to an animal-carcass incineration plant, where it is shredded to pulp in so-called crushers for 20 minutes at a pressure of 3 bar and a temperature of 133° C. The product is then dried to evaporate off two-thirds of the moist weight. The dry material is then pressed to separate the fat from the protein, and the finished products are returned to the economy in powdered, solid-block or liquid form.

Meat and bone meal has a calorific value of 16 000 to 22 000 kJ/kg. That is nearly equal to the calorific value of lignite (approx. 23 500 kJ/kg). It also contains very little heavy metals – far less than in normal coal.

3.5 Dried sewage sludge

Dried sewage sludge, which is generated in dedicated drying facilities in order to reduce the volume of waste flow, also can be employed as an alternative fuel.

4 Gaseous fuels [32–56]

Biogas, like landfill and sewage gas, is a metabolite of methane bacteria. Biogas evolution is a very frequent occurrence in nature. It takes place wherever biomass is digested by microorganisms under anaerobic conditions (e.g., in swamps, in the mud at the bottom of lakes and ponds, and in the digestive tracts of animals). In the process, some of the energy stored via photosynthesis is released in the form of methane, CH_4. At the same time, complex organic compounds are biodegraded, and the resultant decomposition products become directly available as phytonutrients. Such biological degradation processes take place during the anaerobic fermentation of organic material in municipal, commercial and industrial waste and in animal der Natur weit verbreiteter Vorgang, der überall dort stattfindet, wo Biomasse von Mikroorganismen unter anaeroben Bedingungen im feuchten Milieu abgebaut wird (z. B. in Sümpfen, im Grundschlamm von Gewässern und im Pansen oder Darmtrakt von Tieren). Die durch die Fotosynthese gespeicherte Sonnenenergie wird dabei zum Teil in Form von Methan CH_4 freigesetzt. Gleichzeitig werden komplexe organische Verbindungen abgebaut. Die Abbauprodukte stehen unmittelbar als Pflanzennährstoff zur Verfügung. Diese biologischen Abbauprozesse finden bei der anaeroben Vergärung von organischen Stoffen aus Siedlungs-, Gewerbe-, Industrieabfällen und in der Viehwirtschaft statt. Bei gasförmigen Bioenergieträgern sind Deponiegas, Klärgas und landwirtschaftliches bzw. sonstiges Biogas aus organischen Abfällen sowie Synthesegas aus der Vergasung fester Biomasse zu unterscheiden. Wie nachfolgend erläutert, ist aus kommunaler Sicht ausschließlich Biogas eine mögliche Option für eine Wärme- und/oder Strombereitstellung. Durch die Produktion und Nutzung von Biogas kann ein Beitrag zur Lösung des kommunalen Problems der Entsorgung von organischen Abfällen geleistet werden. Bei der Vergärung dieser Abfälle wird – anders als bei der alternativ möglichen Kompostierung – zusätzlich Energie erzeugt. Zusätzlich lassen sich weitere organische Substrate, wie z. B. organische Rückstände aus der Landwirtschaft und Haushaltsabfälle, aus technischer Sicht, in idealer Weise ergänzend einsetzen, sodass hier neue lokale Kooperationen denkbar sind.

4.1 Deponiegas

Müll enthält organische Substanzen, die bei der Deponierung in verschiedenen Stufen der Zersetzung durch Mikroben abgebaut werden. Die Endprodukte sind Methan (CH_4) mit 45 bis 65 Vol.-%, Kohlendioxid (CO_2) mit 25 bis 35 Vol.-% und Stickstoff (N_2) mit 10 bis 20 Vol.-%; rund 2 Vol.-% entfallen auf andere Inhaltsstoffe wie Geruchs- und Spurenstoffe (Halogenwasserstoffe, Schwefelwasserstoff, Kohlenmonoxid, Quecksilber usw.). Diese Stoffe können zur Korrosion in Aufbereitungsanlagen und Motoren führen. Die Gasbildung wird von einer Reihe von Faktoren beeinflusst: Deponiematerial, Lagerungshöhe und Dichte des Deponiematerials, Wassergehalt, Lufttemperatur, Atmosphärendruck und Niederschlagsmenge. Der Zersetzungsprozess in einer Deponie mit nennenswerter Gasentstehung dauert etwa 15 bis 25 Jahre, die Gasmenge nimmt dabei kontinuierlich ab. Aus einer Tonne Müll entstehen insgesamt etwa 150 bis 200 Nm^3 Deponiegas mit einem Methangehalt von rund 50 bis 60 %, was einer Energiemenge von ca. 100 l Heizöl entspricht. Der Heizwert von 2,5 m^3 Deponiegas entspricht hierbei etwa dem von 1 l Heizöl. Bei einer Verbrennung können Schadstoffe freigesetzt bzw. gebildet werden. Besonders hervorzuheben sind hier Dioxine und Furane, polycyclische aromatische Kohlenwasserstoffe (PAK) und höhere Kohlenwasserstoffe.

Um die Entstehung dieser Stoffe zu vermeiden, sind Verbrennungstemperaturen von mindestens 1 200 °C erforderlich.

4.2 Klärgas

Auch bei der biologischen Abwasserbehandlung in Kläranlagen entstehen brennbare Gase. Bei der Reinigung des Abwassers zurückgehaltene Stoffe werden in anaeroben Prozessen durch Bakterien in Faultürmen teilweise zersetzt. Endprodukte sind ausgefaulter Klärschlamm und Klärgas, wobei letzteres in etwa mit Deponiegas verglichen werden kann.

4.3 Landwirtschaftliches Biogas (Methan)

Landwirtschaftliches Biogas kann sowohl über Fermentati-

Tabelle 2: Brennstoffzusammensetzung von Holz [Nussbaumer 1994]
Table 2: Chemical composition of fuelwood [Nussbaumer 1994]

Kohlenstoff/Carbon (C) [g/kg]	490
Wasserstoff/Hydrogen (H) [g/kg]	60
Sauerstoff/Oxygen (O) [g/kg]	440
Stickstoff/Nitrogen (N) [mg/kg]	900
Schwefel/Sulphur (S) [mg/kg]	120
Chlorid/Chloride (Cl) [mg/kg]	<0.01
Cadmium/Cadmium (Cd) [mg/kg]	0.11
Zink/Zinc (Zn) [mg/kg]	14.57
Kupfer/Copper (Cu) [mg/kg]	1.3
Fluor/Fluorine (F) [mg/kg]	<0.01
Blei/Lead (Pb) [mg/kg]	0.98
Chrom/Chrome (Cr) [mg/kg]	0.94

husbandry. Among the gaseous sources of bioenergy, differentiation is made between landfill gas, sewage gas and farm gas (or other forms of biogas derived from organic waste), as well as synthetic gas won by the gasification of solid biomass. As explained below, the only form seen, from a municipal viewpoint, as a possible option for generating heat and/or electricity is biogas. The production and use of biogas can help solve one problem faced by most communities: what to do with organic waste. In contrast to the alternative option of composting, the fermentation of waste also generates harnessable energy. Additionally, various other organic substrates in the form of farm residue and household waste, for example, can be added to the process for an ideal supplementation in the technical sense, hence paving the way for new, local forms of cooperation.

4.1 Landfill gas

Garbage contains organic material that goes through various stages of microbial decomposition at the landfill. The end products are methane (CH_4), accounting for 45 to 65 vol.-%, carbon dioxide (CO_2), accounting for 25 to 35 vol.-%, and nitrogen (N_2), accounting for 10 to 20 vol.-%; some 2 vol.-% are made up of diverse other ingredients like odour substances and trace substances (hydrogen halides, hydrogen sulphides, carbon monoxide, mercury, etc.). Such substances can cause corrosion in conditioning equipment and motors. Gas evolution is influenced by a number of factors, including for example, the type of material contained in the landfill, the depth of the tip, the density of the tipped material, the water contents, the ambient temperature, the atmospheric pressure and the precipitation rate. The decomposition process in a landfill generating significant amounts of gas lasts about 15 to 25 years. The volume of gas decreases steadily over this period of time. A ton of garbage produces a total of around 150 to 200 Nm^3 of landfill gas with a methane content of about 50 to 60%. This is approximately equivalent to the amount of energy contained 100 litres of heating oil, with the calorific value of 2.5 m^3 landfill gas corresponding to that of roughly 1 litre of heating oil. Combustion of the gas can release or form pollutants, of which dioxins and furans, polycyclic aromatic hydrocarbons (PAC) and higher hydrocarbons are the most prominent. It takes combustion temperatures of at least 1 200° C to prevent the formation of such substances.

4.2 Sewage gas

Combustible gases are also generated in the biological

onsprozesse (Biogas) als auch thermochemisch aus Biomasse hergestellt werden. Mehr als 2/3 der landwirtschaftlichen Biogasanlagen arbeiten mit Rindergülle, der Rest überwiegend mit Schweinegülle. Nur wenige Anlagen sind für Hühnergülle gebaut worden. Bau und Betrieb einer Biogasanlage im landwirtschaftlichen Bereich können mittlerweile als verhältnismäßig risikolos angesehen werden.

4.4 Industrielles Biogas (Methan)

Der hauptsächliche Unterschied zwischen den vorgenannten Gassorten und dem in einer industriellen Anlage erzeugten Biogas liegt darin, dass durch eine konsequente Auswahl der zur Vergärung eingesetzten Substrate die Gasqualität beeinflusst werden kann.

5 Flüssige Brennstoffe und Kraftstoffe

Flüssige Bioenergieträger sind geeignet für die energetische Nutzung als Energieträger für eine Wärme- und Strombereitstellung. Eine Brennstoffproduktion, Anbau von Rapssaat und daraus die Erzeugung von Pflanzenöl beispielsweise, ist in Relation zur konventionellen, fossilen Treibstoffherstellung sehr kostenintensiv. Mit Blick auf die derzeitigen durchschnittlichen Verkaufspreise für Rapsöl (etwa 0,65 €/l) erscheint ein Rapsöl-BHKW als Alternative betriebswirtschaftlich unattraktiv. Ein problemloser Einsatz naturbelassener flüssiger Brennstoffe in vorhandenen Energieerzeugungsanlagen erfordert einen zum Teil erheblichen Entwicklungsbedarf sowohl bezüglich der Apparate als auch bezogen auf die Brennstoffqualität. Es fehlen verlässliche Qualitätsregeln für den Brennstoff, sodass ein hoher Kontrollaufwand seitens des Betreibers erforderlich ist. Regenerative Kraftstoffe sind vor allem Alkohole, Kohlenwasserstoffe, Pflanzenöle und Folgeprodukte sowie Tierfett.

Neben der Nutzung in Verbrennungskraftmaschinen ist der Einsatz regenerativer Kraftstoffe für den Betrieb von Brennstoffzellen in mobiler Anwendung und in dezentraler Anwendung als Kraft-Wärme-Kopplungs-Einheit (KWK) eine besondere technologische Herausforderung.

Bis auf den, begrenzt zur Verfügung stehenden, Biodiesel existieren praktisch keine auf dem Markt befindlichen sofort verfügbaren Lösungsansätze für eine „nachhaltige Mobilität" und Diversifizierung auf dem Kraftstoffmarkt. Sowohl für konventionelle Verbrennungsmotoren als auch für zukünftige Brennstoffzellensysteme sind Kraftstoffe erforderlich, die neben den schadstofflimitierten Emissionen eine günstige CO_2-Bilanz aufweisen. Dies kann neben einer Verbrauchsreduzierung längerfristig nur durch regenerativ hergestellte Kraftstoffe und Gase, wie z. B. Methanol und Methan, aus Vergärungsprozessen produziert werden.

5.1 Pflanzenöle und -fette

Diese zählen zu den zukunftsträchtigen Energieträgern. Ihr Einsatz ist dem von fossilen Brennstoffen hinsichtlich des Handlings vergleichbar. Sie eignen sich hervorragend als Ersatz für fossile Brennstoffe in Tunnelöfen oder auch modernen Antriebstechnologien wie Brennstoffzellen oder Verbrennungsmotoren. Der Einsatz ist, auch unter Berücksichtigung des Transportweges, weitgehend CO_2-neutral.

In der Ziegelei Gasser werden Pflanzenöle und Pflanzenfette direkt über die Brenneranlage verfeuert. Die Schwermetallgehalte der pflanzlichen Öle und Fette sind so gering, dass sie im Regelfall nicht quantitativ bestimmt werden können, weil sie unterhalb der Bestimmungsgrenze liegen. Somit sind sie ein ideales Substitut zum Schwer- oder Altöl. Es handelt sich bei

processing of wastewater in sewage treatment plants. Material collected at the mechanical cleaning stage can be partially decomposed via bacteria-based anaerobic processes in tower-type digesters. Here, the end products are digested sludge and sewage gas. Sewage gas and landfill gas are roughly equivalent.

4.3 Farm biogas (methane)

Farm biogas can be produced either by fermentation or extracted from biomass by thermochemical means. More than 2/3 of all agricultural biogas installations run on semi-liquid cattle manure, and the rest run on semi-liquid pig manure. A few plants have been built for semi-liquid chicken manure. The construction and operation of modern biogas plants for agricultural application may be regarded as relatively risk-free.

4.4 Industrial biogas (methane)

The main difference between the types of gas discussed above and the kind of biogas generated in an industrial facility is that the quality of the latter gas can be influenced by systematic selection of fermentation substrates.

5 Liquid fuels

Liquid fuels are well suited for use as energy sources in heat- and power-generating facilities. Fuel production in the form of, say, rapeseed cultivation with subsequent vegetable-oil extraction is very cost-intensive in relation to the production of conventional fossil fuels. Considering the present average market price of rapeseed oil (approx. 0.65 €/l) a rapeseed-fuelled combined heat and power plant (CHP) would hardly appear attractive as an economic alternative. Moreover, for natural liquid fuels to run smoothly in existing power generating facilities, substantial progress will still have to be made in terms of apparatus and fuel quality. Reliable quality criteria are still lacking for such fuels, hence necessitating elaborate control inputs on the part of the operator. The primary renewable-fuel spectrum includes, in addition to hydrogen, various forms of alcohol, hydrocarbons, vegetable oils and their derivatives, and animal fat.

Apart from serving in combustion engines, renewable fuels also make an especially technologically challenging candidate for mobile applications such as fuel cells and decentralized applications like CHPs.

With the exception of biodiesel, the availability of which is also limited, the market has practically no immediately available choices to offer in terms of "sustainable mobility" and fuel diversification. For conventional combustion engines and future fuel-cell systems alike, fuels that emit little pollution and have a good CO_2 balance are what is needed. Apart from reducing consumption, then, the use of renewable fuels and gases like methanol and methane obtained via fermentation processes is the only long-term solution.

5.1 Vegetable oil and fat

These two options are a promising pair of alternative fuels. In terms of handling, they are comparable to fossil fuels, and they make very good substitutes for fossil fuels in tunnel kilns as well as in such modern motive mechanisms as fuel cells and combustion engines. Even considering transportation, their use is extensively CO_2-neutral.

At the brickworks Ziegelei Gasser, vegetable oil and fat are put directly through the burners. Vegetable oil and fat have such den pflanzlichen Flüssigbrennstoffen um CO$_2$-neutrale Brennstoffe.

5.2 Biodiesel [57]

Auch Rapsöl-Methylester (RME) oder Pflanzenöl-Methylester (PME) werden durch eine Umesterung des Pflanzenöls hergestellt, wodurch eine Homogenisierung und die nötige Lagerstabilität erzielt werden. Die Befreiung von der Mineralölsteuer hat in Deutschland einen Biodieselboom ausgelöst, sodass bereits an über 1 000 Tankstellen flächendeckend Biodiesel angeboten wird. Der Marktanteil beträgt etwa 0,55 % auf dem Kraftstoffsektor. Der Kraftstoff kann zu 100 % ohne größere Umstellungen in den meisten herkömmlichen Dieselfahrzeugen eingesetzt werden.

5.3 Bioalkohol/Ethanol

Bioalkohol/Ethanol wird durch die Fermentation zucker- und stärkehaltiger Pflanzen gewonnen. Neben stärkehaltigen Pflanzen sind Zuckerrohr und -rüben die am häufigsten verwendeten Ausgangsmaterialien für die Ethanolproduktion. Während zuckerhaltige Pflanzen direkt vergoren werden, muss bei Getreide, Mais und Kartoffeln die Stärke zunächst enzymatisch in Zucker umgewandelt werden. Ein relativ neues Verfahren ermöglicht den Einsatz von cellulosehaltiger Biomasse für die Ethanolproduktion, was das Potenzial möglicher Einsatzstoffe erheblich erweitert. Beim Einsatz cellulosehaltiger Biomasse, wie Stroh oder Holzhackschnitzel, muss zunächst deren Struktur aufgebrochen werden, was durch Kochen unter Säurezugabe erfolgt. Danach kann die Cellulose durch chemisch-enzymatische Aufschließungsprozesse für die Verzuckerung und Vergärung umgewandelt werden. Lignin fällt als Nebenprodukt bei dem Aufschlussprozess an.

Das erzeugte Bio-Ethanol kann direkt als Kraftstoff in Verbrennungsmotoren eingesetzt werden. In der Praxis wird jedoch kein reines Ethanol verwendet, vielmehr erfolgt eine Beimischung zu konventionellen Otto-Kraftstoffen. Mischungen im Bereich von 5 bis 10 % Ethanolanteil (z. B. E10) können in konventionellen Kfz ohne Umstellung oder Einschränkung eingesetzt werden, was vorwiegend in einigen amerikanischen Bundesstaaten praktiziert wird. Der hohe Sauerstoffgehalt fördert die Verbrennung des Benzin-Ethanol-Gemisches.

Das langfristige Potenzial einer weltweiten Bio-Ethanolproduktion wird mit 500 Mio. t/a für zucker- und stärkehaltige Pflanzen, für cellulosehaltige Biomasse mit der dreifachen Menge angegeben. Das weltweite Produktionspotenzial von Bio-Ethanol wurde mit 1,3 Mrd. t/a angegeben, was einem Äquivalent von 37 % des Erdölverbrauchs von 1998 entspricht.

5.4 Tierfett

Tiermehl und Tierfett werden in Tierkörperbeseitigungsanstalten (TBA) aus Schlachtabfällen und verendeten Tieren gewonnen. Bis vor dem Auftreten der ersten BSE-Fälle waren Tiermehl und Tierfett Produkte mit wirtschaftlichem Wert. Sie dienten z. B. als Futterzusatz bei der Schweinemast. Erst durch Verbot des Verfütterns, des innergemeinschaftlichen Verbringens und der Ausfuhr sind Tiermehl und Tierfett zu Abfällen geworden. In der EU fallen jährlich ca. 7 000 000 t Tiermehl und ca. 3 100 000 t Tierfett an. Alle hergestellten Tiermehle und Tierfette werden bei 133 °C und einem Druck von 3 bar über einen Zeitraum von 20 Minuten drucksterilisiert. Durch dieses Verfahren ist eine Abtötung aller Bakterien und Keime garantiert. Nach der Drucksterilisation wird das Material entwässert und separiert. Durch die Separation entstehen Tiermehl und Tierfett.

miniscule heavy metal contents, that they usually are not even quantifiable, i.e., they are situated below the limit of quantization. This makes them an ideal substitute for heavy oil and waste oil. Phytogenic liquid fuels are CO$_2$-neutral.

5.2 Biodiesel [57]

Rapeseed methyl ester (RME) and vegetable-oil methyl esters (VME) in general are obtained by transesterification of vegetable oil, the goal being to homogenize the oil and improve its storage stability. Exemption from mineral-oil taxation in Germany triggered a biodiesel boom that has already given rise to a close-knit network of more than 1 000 biodiesel filling stations. Biodiesel presently commands a roughly 0.55% share of the fuel market. This kind of fuel can be used "straight" in most conventional-type diesel engines with no major conversions.

5.3 Bioalcohol/ethanol

Bioalcohol/ethanol is obtained from the fermentation of saccharine (sugary) and/or amylaceous (starchy) plants. Hence, starchy plants and sugar cane/beets are the most frequently employed starting materials for ethanol production. While sugar plants can be directly fermented, the starch in grain, maize and potatoes first has to be enzymatically converted into sugar. A relatively new process now enables the use of cellulosic biomass for producing ethanol – a fact that substantially expands the range of potential feedstock. However, before cellulosic biomass (straw, wood chips, ...) can be fermented, it first has to be broken down by boiling in an acid solution. After that, the cellulose can be converted into sugar and fermented by way of chemical-enzymatic digestion processes. Lignin occurs as a byproduct of the digestive decomposition process.

Thusly obtained bioethanol can serve directly as fuel for combustion engines. In actual practise, however, ethanol is not used "straight" but mixed into conventional carburettor fuels. Blends containing 5% to 10% ethanol (e.g., E10) can be used in conventional motor vehicles without conversion or limitation, as mainly practised in some parts of the U.S.A. The high oxygen content promotes combustion of the petrol/gasoline-ethanol mixture.

The long-term potential of global bioethanol production is quoted at 500 mill. t/a for sugary/starchy plants, and three times that much for cellulosic biomass. The global bioethanol production potential reportedly stands at 1.3 billion t/a, which is equivalent to 37% of the world's 1998 oil consumption.

5.4 Animal fat

Meat, bones and fat from animals are obtained from slaughterhouse waste and perished animals. Prior to the first cases of BSE, meat and bone meal and animal fat had economic value. They were used as feed supplements at pig fattening stations, for example. Then, their use as feed, their intra-Community introduction, and their exporting was banned, suddenly turning meat and bone meal and animal fats into refuse. Each year, some 7 000 000 tons of meat and bone meal and roughly 3 100 000 tons of animal fats are generated within the EU. All produced quantities of meat and bone meal are pressure-sterilized at 133° C and 3 bar for 20 minutes. This guarantees that all bacteria and germs are destroyed. Following pressure-sterilization, the material is dewatered and separated into meat and bone meal and animal fats.

Animal fat has a calorific value of roughly 35 000 to 39 000 kJ/kg. This compares favourably with that of heavy oil (41 000 kJ/kg). At Gasser brickworks, animal fat is delivered

Tabelle 3: Eigenschaften der Brennstoffe (Literaturdaten)
Table 3: Fuel characteristics (literature data)

Bezeichnung Designation	Holz und Halmgüter Wood & stem plants	Energiepflanzen Energy plants	Tiermehl Meat + bone meal	Klärschlamm Sewage sludge	Biogas	Pflanzenöl Vegetable oil	Biodiesel	Ethanol/ Bioalkohol Ethanol/ bioalcohol	Tierfett (Mittelwerte) Animal fat (mean values)	Wasserstoff Hydrogen	Methanol	Synth. Kohlenwasserstoffe Synth. hydrocarbons	Bio-Pyrolyseöl Bio-pyrolysis oil	Schweröl (Mittelwerte) Heavy oil (mean values)
Trockenrückstand [%] Dry residue [%]									99.6					ca./approx 99.5
Aschegehalt [%] Ash content [%]	0.5–23.00		22.0–31.0						< 0.11					0.1
Trockenverlust [%] Loss on drying [%]									0.4					0.3
Glühverlust der Trockensubstanz [%] LOI of dry material [%]									95.9					–
Brennwert HU/HO [kJ/kg] Calorific value gross/net [kJ/kg]	18 800– 14 100/ k.A.		15 700/ k.A.	8 000– 11 500/ k.A.					36 350 39 250					40 320/k.A.
Wasserstoff/Hydrogen	5.07–7.7		7.7	3–4					11.32					
Stickstoff/Nitrogen	5.8–10.6		5.8	1.9–6	0–5				0.32					
S Fluoride [mg/kg] S Fluorides [mg/kg]				k.A.					< 1 000					
S Chlor/Chlorine				0.05–0.4					< 200					
Gesamtschwefel [%] Total sulphur [%]		0.33–0.62	0.5	0.5–1.3	0–1				< 0.10					1.0
Quecksilber [mg/kg] Mercury [mg/kg]			0.18	2.3					<0.10					
Kohlenstoff [%] Carbon [%]			37.2	22–31					73.32					
Antimon/Antimony									< 20					
Arsen/Arsenic			0.3						< 20					
Blei/Lead			4.25	200–390					< 20					
Cadmium/Cadmium			0.43	3.6–4.3					< 2					
Chrom/Chrome			8.31	64–72					< 3					
Kupfer/Copper				322					< 3					
Nickel									< 3					250
Vanadium									< 20					

Bezeichnung Designation	Holz und Halmgüter Wood & stem plants	Energiepflanzen Energy plants	Tiermehl Meat + bone meal	Klärschlamm Sewage sludge	Biogas	Pflanzenöl Vegetable oil	Biodiesel	Ethanol/ Bioalkohol Ethanol/ bioalcohol	Tierfett (Mittelwerte) Animal fat (mean values)	Wasserstoff Hydrogen	Methanol	Synth. Kohlenwasserstoffe Synth. hydrocarbons	Bio-Pyrolyseöl Bio-pyrolysis oil	Schweröl (Mittelwerte) Heavy oil (mean values)
Thallium									< 20					
Zink/Zinc			140						430					
Zinn/Tin									< 20					
Mangan/Manganese									6					

In der Übersicht wurde auf Literaturdaten, teilweise ergänzt durch eigene Messungen, zurückgegriffen. Gegebenenfalls wurden die Werte umgerechnet.
The above survey is based on literature data supplemented by in-house readings. Where necessary, the data was converted.

at a temperature of approx. 80°C in temperature-controlled trucks and pumped from the trucks into a heated, insulated tank. The fat serves directly as fuel for the existing combustion equipment. Its heavy-metal content is so low as to be normally unquantifiable (i.e., it is situated below the limit of quantization). Hence, animal fat makes an ideal substitute for heavy oil and used oil.

5.5 Hydrogen

Hydrogen cannot be considered a fuel unless and until it can be obtained from renewable sources of energy with reasonable efficiency. Hydrogen is excellently suited for use in modern motive-power engineering applications. Hydrogen does have its drawbacks, though, i.e., specifically its infrastructural requirements for storage and transportation.

5.6 Methanol

Methanol could eventually gain significant importance as fuel. In combustion engines, methanol increases engine efficiency while reducing emissions to below the levels generated by pure petrol/gasoline. Adding methanol to conventional fuel is also an interesting option. In fuel cells, methanol can either be used directly (direct methanol fuel cells) or first converted to hydrogen in an on-board reformer for subsequent power generation in a fuel cell serving an electric motor. Such vehicles offer the double benefit of using liquid fuel but still emitting practically no pollutants.

Other possibilities include the use of methanol as a starting material for producing substitute fuels for diesel (together with vegetable oils) and for making octane boosters (MTBE).

Methanol has one decisive disadvantage in comparison with conventional types of fuel: it is a liquid, but it is also aggressively corrosive, so it can not be marketed through the same channels as petrol/gasoline and diesel (unlike various grades of petrol/gasoline/diesel/jet-propulsion fuel). The world's presently largest initiative for introducing methanol as an alternative fuel is taking place in California, where approx. 15 000 vehicles are operating on M85 (a blend of 85% methanol and 15% gasoline). A few car makers (including Ford) are building commercial M85 vehicles, and numerous other manufacturers have developed "flexible-fuel vehicles" that can run on either methanol or normal gasoline. Most large-scale methanol production is based on extracting it from natural gas at an efficiency level of about 70%. The main focus of the U.S. methanol program is to reduce emissions in population centres with accordingly heavy traffic. However, in order to actually achieve any reduction in CO_2 emissions, the methanol would have to be obtained from renewable resources.

5.7 Synthetic hydrocarbons (designer fuels)

Fuels belonging to this category are produced according to the Fischer-Tropsch process as mixtures of H_2, CO and CO_2. The product is referred to as synthetic gas and can be obtained via thermochemical conversion of biomass, with subsequent purification and conditioning. The Fischer-Tropsch process was developed as a means of gasifying coal and served during World War II as a source of synthetic fuels. High-quality diesel-like fuel can be made from the synthetic gas. While liquid fuels based on natural gas cost roughly the same as crude-oil distillates, products based on biomass are considerably more expensive, because additional steps of processing are necessary. Liquid fuels obtained via Fischer-Tropsch synthesis can make direct use of the existing diesel-fuel infrastructure. FT diesel contains no sulphur or aromatics, and it is transportable,

Tierfett hat einen Heizwert von ca. 35 000 bis 39 000 kJ/kg. Das entspricht in etwa dem Heizwert von Schweröl mit 41 000 kJ/kg. Im Ziegelwerk Gasser wird das Tierfett mit einer Temperatur von ca. 80 °C in Thermozügen per Lkw angeliefert und über Rohrleitungen in einen isolierten und beheizten Tank gefördert. Das Fett wird über die bestehende Brenneranlage verfeuert. Die Schwermetallgehalte des Tierfetts sind so gering, dass sie im Regelfall nicht quantitativ bestimmt werden können, weil sie unterhalb der Bestimmungsgrenze liegen. Somit ist Tierfett ein ideales Substitut zum Schwer- oder Altöl.

5.5 Wasserstoff

Wasserstoff ist kein Energieträger, sofern es nicht gelingt, ihn mittels akzeptablen Wirkungsgrades aus regenerativen Energiequellen herzustellen. Wasserstoff eignet sich hervorragend zum Einsatz in modernen Antriebstechnologien wie Brennstoffzellen, aber auch für Verbrennungsmotoren. Die Nachteile von Wasserstoff sind jedoch die Infrastrukturerfordernisse für Speicherung und Transport.

5.6 Methanol

Methanol könnte zukünftig eine erhebliche Bedeutung als Kraftstoff zukommen. In Verbrennungsmotoren steigt durch die Verwendung von Methanol der motorische Wirkungsgrad bei verringerten Emissionen gegenüber reinem Benzinbetrieb. Auch die Beimischung von Methanol zu konventionellen Kraftstoffen ist eine interessante Option. In Brennstoffzellen kann Methanol entweder direkt (Direkt-Methanol-Brennstoffzelle) verwendet werden oder es wird an Bord des Fahrzeuges zu Wasserstoff reformiert, der in einer Brennstoffzelle zu Elektrizität umgesetzt wird, um einen Elektromotor anzutreiben. Vorteile dieser Fahrzeuge sind die Beibehaltung flüssiger Kraftstoffe und der praktisch schadstofffreie Betrieb.

Weitere Möglichkeiten sind die Verwendung von Methanol als Edukt zur Produktion von Dieselersatzkraftstoffen (zusammen mit Pflanzenölen) und die Herstellung von Oktanboostern (MTBE).

Gegenüber konventionellen Kraftstoffen hat Methanol einen entscheidenden Nachteil: Methanol ist zwar flüssig, kann jedoch auf Grund korrosiver Eigenschaften nicht wie Benzin- und Dieselkraftstoffe über die bestehenden Verteilungsstrukturen vertrieben werden (im Gegensatz zu verschiedenen Qualitäten von Benzin/Diesel/Flugturbinenkraftstoff). Die weltweit größte Initiative zur Einführung von Methanol als Alternativkraftstoff läuft in Kalifornien, wo zurzeit ca. 15 000 Fahrzeuge mit M85 (Gemisch aus 85 % Methanol und 15 % Benzin) betrieben werden. M85-Fahrzeuge werden von einigen Automobilherstellern kommerziell angeboten (z. B. Ford), viele andere Hersteller haben ebenfalls „Flexible Fuels Vehicles" entwickelt, die neben Methanol auch mit normalem Benzin betankt werden können. Großtechnisch erfolgt die Methanolbereitstellung bislang aus Erdgas mit einem Wirkungsgrad von ca. 70 %. Der Schwerpunkt des Methanolprogramms in den USA liegt in der Emissionsminderung in verkehrsbelasteten Ballungsräumen. Soll eine CO_2-Minderung erzielt werden, müsste das Methanol aus regenerativen Ressourcen hergestellt werden.

5.7 Synthetische Kohlenwasserstoffe (designer fuels)

Diese werden nach dem Fischer-Tropsch-Verfahren aus Synthesegas (Mischung aus H_2, CO und CO_2) hergestellt. Das Synthesegas kann durch thermochemische Umwandlung mit anschließender Gasreinigung und -konditionierung aus Biomasse hergestellt werden. Das Fischer-Tropsch-Verfahren stammt aus der Kohlevergasung, wobei im Zweiten Weltkrieg bereits

storable and biologically degradable.

5.8 Bio-pyrolysis oil

Bio-pyrolysis oil is made from biomass according to the flash- or fast-pyrolysis process. Finely shredded biomass is brought into contact with a thermal medium (hot sand) in the absence of air, causing the volatile constituents (some 75% of the total organic solids content of wood) to spontaneously pass to the gas phase. As a rule, technical implementation is based on either a bubbling fluidized bed (BFB) approach or on a process referred to as the "rotating cone". Both methods employ a temperature of 500° C, a maximum of 2 s at peak temperature, and rapid cooling of the pyrolysis gases. The energetic yield ranges between 70 to 80%. The product (bio-pyrolysis oil) is a pungent brown liquid with a calorific value of approx. 14 to 18 MJ/kg, or about half that of extra-light (class-D) fuel oil, with which it is comparable in terms of transportation, storage and use.

6 Conclusions

Only vegetable and animal fats and biogas produced in dedicated facilities can be shortlisted as candidate fuels (= readily available and renewable) for brickworks. All other fuels are unsuitable for various technical, regulatory and/or economic reasons:

- **Wood:** Preparing wood for use as fuel at a brick factory would be very complicated and expensive
- **Stem plants:** The same applies here as that said of wood
- **Energy plants:** Again, the same applies here as that said of wood
- **Meat and bone meal:** Meat and bone meal could be injected into the firing channel as a co-fuel, but the resultant ashes would be a problem to dispose of, and they would diffuse and settle on the bricks
- **Landfill gas:** Past experience with landfill gas at British and Spanish brickworks has been largely negative; corrosion problems were encountered. It basically holds that both quality and yield are highly landfill-specific in that they depend on, among other factors, the nature of the waste material
- **Sewage gas:** Sewage gas would be rarely available
- **Farm biogas (methane):** Before farm gas could be used as fuel, the problem of its high sulphur content and the question of what to do with the digested residue would have to be solved
- **Industrial biogas (methane):** This would constitute an alternative within the scope of a major investment
- **Vegetable oil:** Probably the only reasonable alternative; its use as a fuel for existing facilities would be feasible without need of major conversions or additions
- **Biodiesel:** Its price is not competitive
- **Bioalcohol/ethanol:** Its price is not competitive
- **Animal fats:** Suitable for use as fuel in existing facilities with no major conversions or additions, but complicated regulatory requirements
- **Hydrogen:** Unavailable
- **Methanol:** Unavailable
- **Synthetic hydrocarbons (designer fuels):** Unavailable.
- **Bio-pyrolysis oil:** Unavailable

Literature

Please refer to German text.

Kraftstoffe hergestellt wurden. Aus dem Synthesegas kann dieselähnlicher Kraftstoff hoher Qualität hergestellt werden. Während die aus Erdgas hergestellten flüssigen Kraftstoffe preislich im Bereich von Erdöldestillaten liegen, sind die Produkte auf Biomassebasis auf Grund der zusätzlichen Prozessschritte noch deutlich teurer. Über die Fischer-Tropsch-Synthese erzeugte flüssige Brennstoffe können direkt mit der bestehenden Infrastruktur für Dieselkraftstoff genutzt werden. FT-Diesel ist schwefel- und aromatenfrei, transportabel, lagerungsfähig und biologisch abbaubar.

5.8 Bio-Pyrolyseöl

Bio-Pyrolyseöl wird nach dem Verfahren der Flash- oder Fast-Pyrolyse aus Biomasse hergestellt. Dabei wird fein zerkleinerte Biomasse unter Luftabschluss mit einem Wärmeträger (heißem Sand) in Kontakt gebracht, wobei die flüchtigen Bestandteile (bei Holz ca. 75 % der Trockensubstanz) spontan in die Gasphase übergehen. Zur technischen Realisierung werden in der Regel die Wirbelschicht (meist Bubbling Fluidized Bed [BFB]) oder ein Verfahren namens „Rotating Cone" eingesetzt. Beide Verfahren arbeiten bei einer Temperatur von 500 °C und einer Verweilzeit von max. 2 s mit einer anschließenden schnellen Abkühlung der Pyrolysegase. Die Ausbeute beträgt energetisch 70 bis 80 %. Das Produkt (Bio-Pyrolyseöl) ist eine stechend riechende braune Flüssigkeit mit einem Heizwert von ca. 14 bis 18 MJ/kg, was etwa der Hälfte des Heizwertes von Heizöl extra leicht (HEL) entspricht. Bezüglich Transport, Lagerung und Nutzung ist Bio-Pyrolyseöl jedoch mit HEL vergleichbar.

6 Fazit

Als Brennstoff für die Ziegelei kommen als leicht verfügbare regenerative Brennstoffe ausschließlich pflanzliche und tierische Fette sowie Biogas aus eigens dafür erstellten Anlagen in die engere Auswahl. Alle anderen Brennstoffe sind entweder unter technischen, genehmigungsrechtlichen oder wirtschaftlichen Aspekten nicht darstellbar:

- **Holz:** Die Aufbereitung von Holz für den Einsatz als Brennstoff in der Ziegelei ist sehr aufwändig und kompliziert
- **Halmgut:** Es gelten die Aussagen in Bezug auf Holz
- **Energiepflanzen:** Es gelten die Aussagen in Bezug auf Holz
- **Tiermehl:** Tiermehl könnte als Mit-Brennstoff in den Brennraum eingedüst werden. Ein Problem stellen jedoch die zu entsorgenden Aschen dar, die zudem noch diffus auf den Ziegeln verteilt wären
- **Deponiegas:** Die Erfahrungen mit Deponiegas in Ziegeleibetrieben im Vereinigten Königreich und in Spanien sind eher negativ. Es traten Korrosionsprobleme auf. Allgemein gilt, dass Qualität und Ausbeute sehr deponieabhängig sind, da diese u. a. von der Müllschüttung abhängen
- **Klärgas:** Klärgas steht in der Regel nicht zur Verfügung
- **Landwirtschaftliches Biogas (Methan):** Bei landwirtschaftlichem Güllebiogas ist das Problem des hohen Schwefelanteiles und der Entsorgung der Gärreste zu lösen
- **Industrielles Biogas (Methan):** Im Rahmen einer größeren Investition eine Alternative
- **Pflanzenöl:** Wahrscheinlich die einzige vernünftige Alternative. Als Brennstoff in einer bestehenden Anlage ohne große Umbauten und Einbauten nutzbar
- **Biodiesel:** Preislich nicht konkurrenzfähig
- **Bioalkohol/Ethanol:** Preislich nicht konkurrenzfähig
- **Tierfett:** Als Brennstoff in einer bestehenden Anlage ohne große Umbauten und Einbauten nutzbar, genehmigungsrechtlich kompliziert

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- **Wasserstoff**: Steht nicht zur Verfügung
- **Methanol:** Steht nicht zur Verfügung
- **Synthetische Kohlenwasserstoffe (designer fuels):** Stehen nicht zur Verfügung
- **Bio-Pyrolyseöl:** Steht nicht zur Verfügung

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Ziegelei Gasser Mattonaia GmbH S.r.l., Natz-Schabs (Italien/Italy)

Einsatz von Biogas in der Ziegelei

Der Beitrag beschreibt Versuche zur Biogaserzeugung in einer Ziegelei. Mit dem Gasser-Verfahren können im Prinzip alle organischen Reststoffe ohne Probleme verarbeitet werden. Im Gegensatz zu herkömmlichen Biogasanlagen besteht kein Abwasserproblem, da die organische Substanz im Verfahren vollständig abgebaut wird. Die Fermentationsversuche mit dieser Anlage werden im Oktober 2004 abgeschlossen sein.

Bild 1: Die Ziegelei Gasser befindet sich im landschaftlich sehr reizvollen Südtirol
Fig. 1: Gasser Brickworks is set in the very charming South Tyrolean countryside

Einleitung

Unter dem Sammelbegriff „Erneuerbare Energien“ oder „Regenerative Energien“ sind Energiequellen und Energieträger zusammengefasst, die nach menschlichem Ermessen unerschöpflich sind. Dazu gehören Sonnenenergie, Windenergie, Wasserkraft, Geothermie (Erdwärme), Gezeitenenergie, Biomasse und Biogas. Sie stehen im Gegensatz zu den „erschöpfbaren“ fossilen Brennstoffen Kohle, Erdöl und Erdgas, die heute die Grundlage der Energieversorgung bilden.

In einer Ziegelei bietet sich der Einsatz regenerativer Energiequellen an, da die hauptsächlich verwendeten Tunnelöfen relativ einfache Brennapparate sind, die sich gut an die verschiedensten Brennstoffe und Brennstoffqualitäten anpassen lassen. Der Brennstoffverbrauch einer Ziegelei liegt außerdem in einem Bereich, der für den Einsatz von regenerativen Energien geradezu prädestiniert erscheint.

Abhängig davon, welcher fossile Brennstoff durch Biogas ersetzt wird, kann die vermeidbare Umweltbelastung auf 40 bis 50 TEP (18 bis 22,5 MJ) je 1 000 Tonnen Ziegel geschätzt werden. Dies führt zu einer Reduzierung von ca. 100 bis 200 Tonnen CO_2 je 1 000 Tonnen Ziegel.

Das Verwirklichen ambitionierter Umweltziele verbessert nicht nur die Nachhaltigkeit, reduziert die Umweltbelastung und dient der Produktion selbst, sondern verbessert auch wesentlich die Unternehmensrentabilität. Nachhaltigkeit ist ein wichtiges Verkaufsargument: Der Handel mit CO_2-Zertifikaten sowie

Fritz Mödinger

The utilization of biogas in a brickworks

This report describes tests on biogas generation in a brickworks. In principle, the Gasser method can be used to process all organic residues without any problems. In contrast to conventional biogas plants, this method eliminates the problem of waste water as the organic matter is completely digested in the course of the process. The fermentation tests with this plant will be concluded in October 2004.

Introduction

The generic term "renewable energies" or "regenerative energies" is used to describe energy sources and fuels that are inexhaustible as far as it is humanly possible to judge. These include solar energy, wind energy, hydropower, geothermal power (generated from the heat of the earth), tidal power, biomass and biogas. They contrast with the "exhaustible" fossil fuels coal, mineral oil and natural gas, which form the basis of our energy supply today.

Regenerative energy sources are very suitable for use in brickworks as the commonly installed tunnel kilns are relatively simple firing systems that can be easily adapted to a wide range of different fuels and fuel qualities. Moreover, the fuel consumption of a brickworks is in a range that would seem predestined for the utilization of regenerative energies.

Depending on which fossil fuel is replaced by biogas, the avoidable environmental pollution can be estimated between 40 to 50 TEP (i.e. 18 to 22.5 MJ) per 1 000 tonnes of bricks. This leads to a reduction of around 100 to 200 tonnes CO_2 per 1 000 tonnes of bricks.

The realization of ambitious environmental aims not only improves sustainability, reduces environmental pollution and serves the production operation itself, but enhances business

Bild 2: Gasser produziert Hintermauerziegel
Fig. 2: Gasser produces backing bricks

die Reduzierung der Brennstoffkosten sprechen für den Einsatz von regenerativen Energien als Brennstoff für den Tunnelofen.

Einsatz von Biogas in der Ziegelei

Ausgehend von diesen Überlegungen hat die Ziegelei Gasser ein entsprechendes Forschungs- und Entwicklungsprogramm zum Einsatz von Biogas begonnen.

Biogas ist in der Natur als Sumpfgas, Moorlichter, aber auch in den Mägen von Wiederkäuern zu finden. Dort läuft unter optimalen Bedingungen eine Folge symbiotisch aufeinander abgestimmter Fermentationen ab. Dabei baut eine Vielzahl von Mikroorganismen die Pflanzenteile ab, die als Futter von den Tieren aufgenommen wurden. Ziel ist es, die pflanzlichen Gewebe und Bestandteile für die Tiere als Nahrung verdaulich zu machen. Selbstverständlich ernähren sich die beteiligten Bakterien auch aus diesen Substraten und bauen sie unter gegebenen Bedingungen durch den Stoffwechsel ab.

Die am Markt operierenden Anbieter von Biogasanlagen stellen Anlagen her, die für den Einsatz in einer Ziegelei ungeeignet sind. Von keinem Anbieter werden umsetzbare Lösungen angeboten, was mit den Rückständen nach der Fermentation geschehen soll. In der Regel ist es für einen Ziegeleibetrieb nicht möglich, die Fermentationsreste auf landwirtschaftlichen Flächen auszubringen, wie es bisher üblich war.

In den Versuchen sollte ein Anlagenkonzept entwickelt werden, das in einer Ziegelei sinnvoll eingesetzt werden kann. Dieses Ziel wurde, wenn auch nicht in der ersten Phase der Versuche, erreicht.

Erste Fermentationsversuche

Im Jahr 2002 führte die Ziegelei Gasser in Natz-Schabs in der Nähe von Brixen (Südtirol, Italien) erste Fermentationsversuche mit verschiedenen Substraten durch. Dazu wurde eine einfache, aus zwei Überseecontainern bestehende, Versuchsanlage eingesetzt (Bild 3). Diese Versuche liefen über einen Zeitraum von fünf Monaten. Das anfallende Biogas wurde als Brennstoff im Tunnelofen eingesetzt.

Die einzelnen Bestandteile der Versuchsanlage sind in Tabelle 1 aufgeführt.

Tabelle 1: Komponenten der 1. Versuchsanlage

Zuführung	Aufgabeschurre: 2 m³ Propellermischer: 1,5 kW, 900 U/min Exzenterschneckenpumpe notwendige Rohranlage
Fermenter	Volumen: 48 m³ Einwellenhorizontalmischer: 3 kW mit beheizter Mischerwelle und Wasser: Wasser-Wärmetauscher zum Beheizen der Mischerwelle notwendige Rohranlage
Gasspeicher	Flexibler PVC-Sack mit einem Volumen von ca. 30 m³
Mess-/Steuer- und Regelungstechnik	Aufgabemengenmesser Gasmesser Automatische Gasanalyse Temperatursensoren
Verdichter	Rotationsverdichter, ungekühlt mit Rücklauf notwendige Rohranlage
Brenner	Gezündete Brennergruppe mit 8 Feuerstellen und einem Stundenverbrauch von ca. 25–30 m³ Biogas Steuer- und Regeleinrichtungen Sicherungsvorkehrungen notwendige Rohranlage

Bild 3: Die erste Versuchsanlage bestand aus zwei Überseecontainern

Fig. 3: The first test plant consisted of two overseas containers

profitability too. Sustainability is an important sales argument: trade with CO_2 certificates and the reduction in fuel costs are points in favour of the utilization of regenerative energies as fuel for tunnel kilns.

Utilization of biogas in a brickworks

On the basis of these considerations, Gasser Brickworks has initiated a dedicated research and development programme on the utilization of biogas.

Biogas is found in nature as marsh gas and marsh lights, but also in the stomachs of ruminants. There, under optimum conditions, a series of symbiotically coordinated fermentation processes takes place. In the course of these fermentation processes, a myriad of microorganisms digest the vegetable matter that the animals have eaten as food. These microorganisms make the vegetable tissue and constituents digestible as food for the animals. Naturally, the bacteria themselves feed on these substrates and digest these in metabolic processes.

The biogas plants constructed by those suppliers currently active on the market are not suitable for use in a brickworks. None of the suppliers offers any feasible solution for handling the fermentation residue. It is generally not possible for a brickworks to spread the fermentation residue on agricultural land, which has been common practice up to now.

The aim of the tests was to develop a plant concept that can be usefully implemented in a brickworks. This aim has been achieved, although not in the first phase of the tests.

Table 1: Components of the first test plant

Feed	feed chute: 2 m³ propeller agitator: 1.5 kW, 900 rpm eccentric worm pump necessary pipe system
Fermenter	volume: 48 m³ single-shaft horizontal mixer: 3 kW with heated mixing shaft and water: water heat exchanger for heating the mixing shaft necessary pipe system
Gas storage	flexible PVC bag with a volume of approx. 30 m³
Measurement and control system	feed flow meter gas meter automatic gas analysis temperature sensors
Compressor	rotary compressor, non-cooled with return flow necessary pipe system
Burners	ignited burner group with eight fireboxes and an hourly consumption of approx. 25–30 m³ biogas measurement and control system safety appliances necessary pipe system

Das Substrat wird in die Aufgabeschurre gegeben und von dort in regelmäßigen Zeitabständen von ca. 4 Stunden in den Fermenter gepumpt. Die mittlere Verweilzeit des Substrates im Fermenter beträgt 25 Tage.

Prozesstechnisch entspricht diese Anlage in etwa dem Stand der Technik der auf dem Markt angebotenen und in Betrieb befindlichen Biogasanlagen, die nach dem nassen Verfahren arbeiten. Die biologischen Prozesse finden, unter jeweils nicht optimalen Bedingungen, in einem einzelnen Fermenter ohne räumliche Trennung statt. Getrennt wird nur nach den unterschiedlichen Dichten des Substrates, die sich während des Prozessverlaufes ergeben und zu einer diffusen Pfropfenströmung von der Einlassseite in Richtung Auslassseite im Fermenter selbst führen.

Ziel dieser Versuche war es, Erfahrungen hinsichtlich des Einsatzes von Biogas in einem Tunnelofen und der Verwendung der Fermentationsreste (ca. 2,5 Masse-% bezogen auf die Trockensubstanz des Aufgabegutes) zu sammeln.

Tabelle 2: Überblick über verschiedene in Labor- und Pilotversuchen getestete Biomassen
Table 2: Overview of the different biomasses used in laboratory and pilot-scale tests

Biomasse/biomass	$m^3/kg_{Trockensubstanz}$ $m^3/kg_{dry\ substance}$
Küchenreste/kitchen waste	0.7–1.3
Kompostierbare Verpackungen compostable packaging	0.64
Fertiggerichte und Reste aus der Lebensmittelherstellung/convenience foods and waste from food production	0.32–0.8
Schlachtreste/slaughterhouse waste	0.34–0.71
Organische Öle einschließlich Schmieröle organic oils including lubricants	> 0.5
Fischereireste/fishery waste	≈ 0.5
Bioabfälle aus Getrenntsammlung biowaste from separate collections	0.40–0.58
Kartoffelreste/potato waste	≈ 0.48
Destillationsreste/still bottoms	≈ 0.46
Biertrester/beermaking residues	0.42–0.5
Obstdestillationsreste/fruit distillation residue	0.45
Grünschnitt und Grünabfälle/green cuttings and waste	0.35–0.46
Papierschlamm und Papierreste paper sludge and paper residues	0.2–0.3

Eingesetzte Biomassen

Tabelle 2 zeigt einen Überblick über die verschiedenen in Labor- und Pilotversuchen getesteten Biomassen. Im Rahmen der Pilotversuche wurden nur solche Substrate verwendet, bei denen davon ausgegangen werden konnte, dass die anfallenden Fermentationsreste problemlos als Porosierungsstoffe bei der Ziegelproduktion eingesetzt werden können. Gülle wurde von vornherein wegen der bekannten Probleme mit der Zusammensetzung des Biogases, des hohen Schwefelgehaltes und der Fermentationsrückstände von den Versuchen ausgeschlossen.

Die chemische Zusammensetzung des Biogases ist in Tabelle 3 dargestellt.

Biogas als Brennstoff

Die Tagesbiogasproduktion der Versuchsanlage betrug ca. 30 m³. Damit konnte eine Brennergruppe über einen Zeitraum von ca. 10 bis 14 Stunden in der Ziegelei Gasser betrieben werden. Das in der Versuchsanlage anfallende Gas wurde

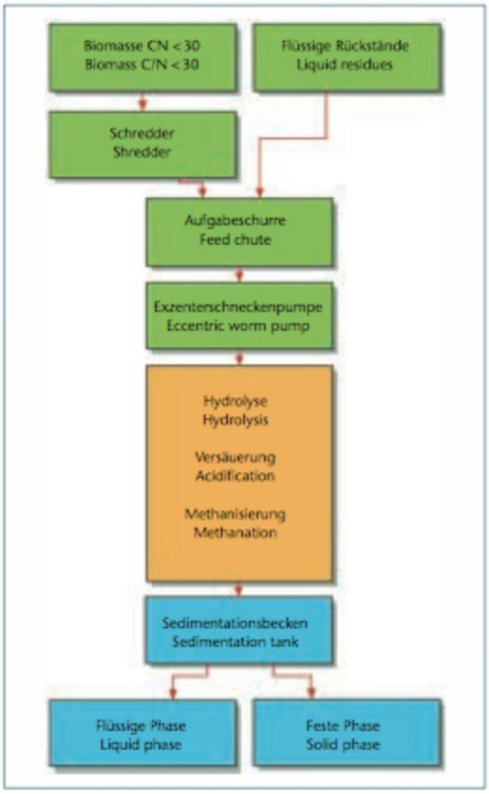


Bild 4: Verfahrensschema der 1. Fermentationsanlage
Fig. 4: Process flow of the first fermentation plant

Initial fermentation tests

In 2002, Gasser Brickworks in Natz-Schabs, near Brixen (Southern Tyrol, Italy), conducted its first fermentation tests with different substrates. For this purpose, a simple test plant consisting of two overseas containers was used (Fig. 3). These tests ran over a period of five months. The biogas produced was used as fuel in the tunnel kiln.

The individual components of the test plant are listed in Table 1. The substrate is placed into the feed chute, and from there pumped into the fermenter at regular intervals of around four hours. The average residence time of the substrate in the fermenter was 25 days.

In respect of the fermentation process, this plant roughly corresponds to the state-of-the-art, wet-process-based biogas plants currently available on the market and operating in the field. The biological processes take place, in sub-optimal conditions, in a single fermenter without any spatial partition. Separation is only performed based on the different densities of the substrate that result during the process and lead to a diffuse plug flow from the inlet side in the direction of the outlet side in the fermenter itself.

The aim of these tests was to collect experience on the utilization of biogas in a tunnel kiln and the use of the fermentation residue (around 2.5 per cent by mass relative to the dry substance of the feed material).

im Tunnelofen des Ziegelwerkes Gasser als Brennstoff eingesetzt. Die Volumina waren für einen kontinuierlichen Betrieb nicht ausreichend. Deshalb fanden die Brennversuche nur während einiger Stunden der Tagschicht statt. Abgesehen von gelegentlichen Zündproblemen, bedingt durch Kondensation, waren keine Schwierigkeiten zu verzeichnen.

Nach Abschluss der Versuche wurden die eingesetzten Brenner auf Korrosion und Verschleiß von Seiten der Herstellerfirma untersucht. Es ergaben sich keine besonderen Verschleiß- oder Abnutzungserscheinungen.

Tabelle 3: Chemische Zusammensetzung des Biogases (Mittelwert aus allen Versuchen)

Table 3: Chemical composition of the biogas (mean values from all tests)

Zusammensetzung/composition	[%]
Methan/methane CH_4	40–75
Kohlendioxid/carbon dioxide CO_2	25–55
Wasserdampf/water vapour H_2O	0–10
Stickstoff/nitrogen N_2	0–5
Sauerstoff/oxygen O_2	0–2
Wasserstoff/hydrogen H_2	0–1
Ammonium/ammonium NH_4	0–1
Schwefelwasserstoff/hydrogen sulphide H_2S	0–1

Porosierung mit Fermentationsresten

Die maximale Porosierung in der Ziegelei Gasser beträgt 20 Vol.-%. Versuche sollten zeigen, ob diese Menge vollständig über Fermentationsreste zugegeben werden kann, ohne dass dabei Probleme auftreten.

Unterschiede wurden weder im Trocken- noch im Brennverhalten oder bei der Herstellung festgestellt. Die Fermentationsreste wurden mit einem von Gasser patentieren Verfahren vorbehandelt, das auch beim Einsatz von Papierfangstoffen und anderen Reststoffen in der Ziegelei eingesetzt wird und hauptsächlich der Geruchsminderung dient. Durch diese Behandlung erfolgt bei längerer Lagerung eine beschleunigte Mineralisierung organischer Bestandteile durch die Einlagerung von Silizium.

Die Eluatwerte der Ziegel wurden im Vergleich zu porosierten Ziegeln aus der Produktion bestimmt. Die Ergebnisse zeigten, dass die mit Fermentationsresten hergestellten Ziegel etwas geringere Eluatwerte an Schadstoffen aufwiesen als die ohne Fermentationsreste hergestellten. Dies dürfte auf eine bessere Schmelzphasenbildung bei niederer Temperatur zurückzuführen sein. Änderungen im Ausblühverhalten wurden nicht festgestellt, waren aber angesichts der chemischen Analysen Eluat und Feststoff auch nicht zu erwarten.

Fazit

Die Versuche haben ergeben, dass Biogas in einem Ziegeleibetrieb sinnvoll eingesetzt werden kann und der Verwertung der festen Fermentationsreste keine Argumente entgegenstehen. Die flüssigen Fermentationsreste waren jedoch erwartungsgemäß nicht über die Kanalisation zu entsorgen, ohne dass hohe Kosten auftreten. Dafür war die organische Restbelastung zu hoch.

Biogasanlage nach dem Kaskadenprinzip

Basierend auf den Ergebnissen der ersten Versuchsreihe und weiteren Laboruntersuchungen wurde eine Biogasanlage nach dem so genannten Kaskadenprinzip entwickelt. Diese

Biomasses used

Table 2 presents an overview of the biomasses used in various laboratory and pilot-scale tests. In the pilot-scale tests, only those substrates were used that could be assumed to produce fermentation residue suitable for addition to the brick bodies as pore-forming agents. Manure was eliminated from the tests from the very start on account of known problems with the composition of the biogas, the high sulphur content and the fermentation residues.

The chemical composition of the biogas is shown in Table 3.

Biogas as fuel

The daily biogas output of the test plant was around 30 m³. This could be used to operate a burner group over a period of around 10 to 14 hours at Gasser Brickworks. The gas produced in the test plant was used as fuel in the tunnel kiln. The volumes were not sufficient for continuous operation. The firing tests therefore only took place over several hours during the day shift. Apart from occasional ignition problems, which were caused by condensation, no problems were established.

Following conclusion of the tests, the burners used were inspected by their manufacturer for signs of corrosion and wear. No unusual wear or abrasion could be detected.

Tabelle 4: Eigenschaften des Biogases (Mittelwert aus allen Versuchen)

Table 4: Properties of the biogas (mean values from all tests)

Dichte/density [kg/Nm³]	ca./approx 1.2
Unterer Heizwert/net calorific value [MJ/Nm³]/[kcal/Nm³]	14.23–26.80 3.400–6.400
Wasserdampf/water vapour [%]	0–10
Zündtemperatur/ignition temperature [°C]	650–750
Zündkonzentration/ignition concentration [Vol.-%]	6–12
Liter equivalent Heizöl equivalent litres of heating oil [l/Nm³]	0.65–0.56

Pore-formation with fermentation residue

The maximum percentage of pore-forming agents added to the bricks made at Gasser Brickworks is 20 vol. %. Tests were conducted to ascertain whether this quantity can be supplied completely by the fermentation residue without any problems arising. No differences were determined in the drying or the firing behaviour or in the brickmaking process. The fermentation residue was pretreated in a process patented by Gasser, which is also applied when papermaking waste and other waste is processed in the brickworks and is mainly intended to reduce the odour. With this treatment, during longer storage of the waste, the mineralization of the organic matter is accelerated as a result of the uptake of silicon.

The eluate values of the bricks were determined in comparison with porous bricks from the regular production operation. The results showed that the bricks produced with fermentation residue had somewhat lower eluate values than those made without fermentation residue. This can probably be attributed to a better melt phase formation at lower temperatures. Changes in the efflorescence of the bricks were not observed, but considering the chemical analyses of the eluate and solids, these were not expected either.

Conclusions

The tests showed that biogas can be sensibly utilized in a brickworks and there are no arguments against the use of entsprach den Anforderungen von Gasser: eine hohe Gasausbeute bei gleichzeitiger Reduzierung der Kosten für die Einleitung der flüssigen Fermentationsreste und eine geringe Baugröße. Derzeit wird eine Versuchsanlage, basierend auf dem von Gasser patentierten Verfahren, erstellt.

Das Gasser-Verfahren

Im Gasser-Verfahren wird das Substrat (organische Stoffe wie beispielsweise Obsttrester, Filterrückstände aus der Fruchtsaftherstellung, Bioabfälle usw.) fein geschreddert und mittels thermischer, enzymatischer oder thermisch-enzymatischer Hydrolyse aufgeschlossen und der nachfolgenden bakteriellen Methanisierung zugänglich gemacht. Stärkehaltige Stoffe wie beispielsweise Kartoffeln werden vor der Zuführung in die Hydrolyse durch Dämpfen verkleistert.

Hydrolyse

Die Hydrolyse findet bei Temperaturen von 50 °C bis < 100 °C statt.

In der Hydrolyse werden Fette, Saccharosen, Stärken und Eiweißstoffe unter Einwirkung von Wasser gespalten und in eine für die Bakterienkulturen der Biogasanlange leicht verarbeitbare Form überführt.

Eine solche Hydrolyse findet auch in klassischen Biogasanlagen statt, jedoch, wie bereits erwähnt, bei wesentlich geringeren

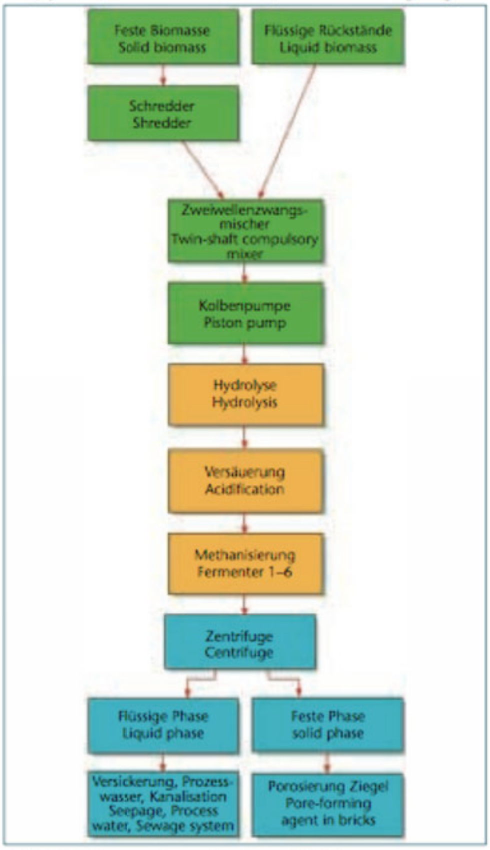


Bild 5a: Verfahrensschema des Gasser-Verfahrens
Fig. 5a: Process flow of the Gasser process

the solid fermentation residues. As expected, however, the liquid fermentation residue could not be disposed of by discharge into the sewage system without high costs being incurred. The residual organic load was still too high to permit this.

Biogas plant based on the cascade principle

Following on from the results of the first series of tests and further laboratory analyses, Gasser developed a biogas plant based on the cascade principle. This met the requirements of Gasser Brickworks, i.e. a compact installation that would enable a high gas yield with a simultaneous reduction in the costs for discharge of the liquid fermentation residue into the sewage system. A test plant based on the Gasser patented process is currently being set up.

The Gasser process

In the Gasser process, the substrate (organic substances such as fruit waste, filter residue from the production of fruit juice, biowaste, etc.) is finely shredded and digested by means of thermal, enzymatic or thermo-enzymatic hydrolysis and made accessible to subsequent bacterial methanation. Starchy substances, such as potatoes for example, are gelatinated by steaming prior to being fed to the hydrolysis process.

Hydrolysis

Hydrolysis takes place at temperatures from 50° C to < 100° C. During hydrolysis, the fats, saccharoses, starches and albuminous (protein) substances are broken down by the action of water and transformed into a substance that can be easily digested by the bacteria cultures in the biogas plant.

A hydrolysis process also takes place in classical biogas plants. In such plants, however, hydrolysis requires lower temperatures and takes a diffuse rather than a specific form.

This specific hydrolysis is one of the special features of the Gasser process. If necessary, in the Gasser process, enzymes or similar or other catalytic substances are added to the feed material during hydrolysis. Recirculated sludge from the plant can also be used for this purpose.

Cascade fermentation

Following hydrolysis, the materials to be fermented are fed to an acidification process under optimally defined thermal conditions. In cascade acidification – similar to in a sewage plant – spe-

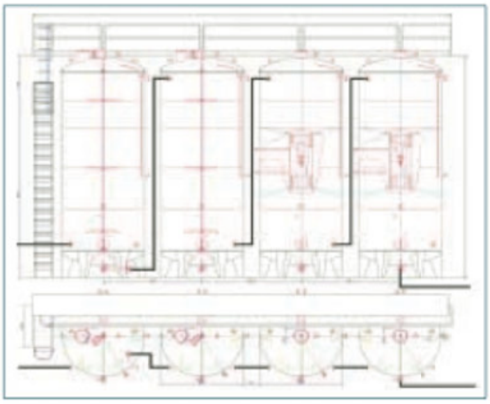


Bild 5b: Technische Zeichnung der Kaskadenanlage
Fig. 5b: Technical drawing of the cascade plant

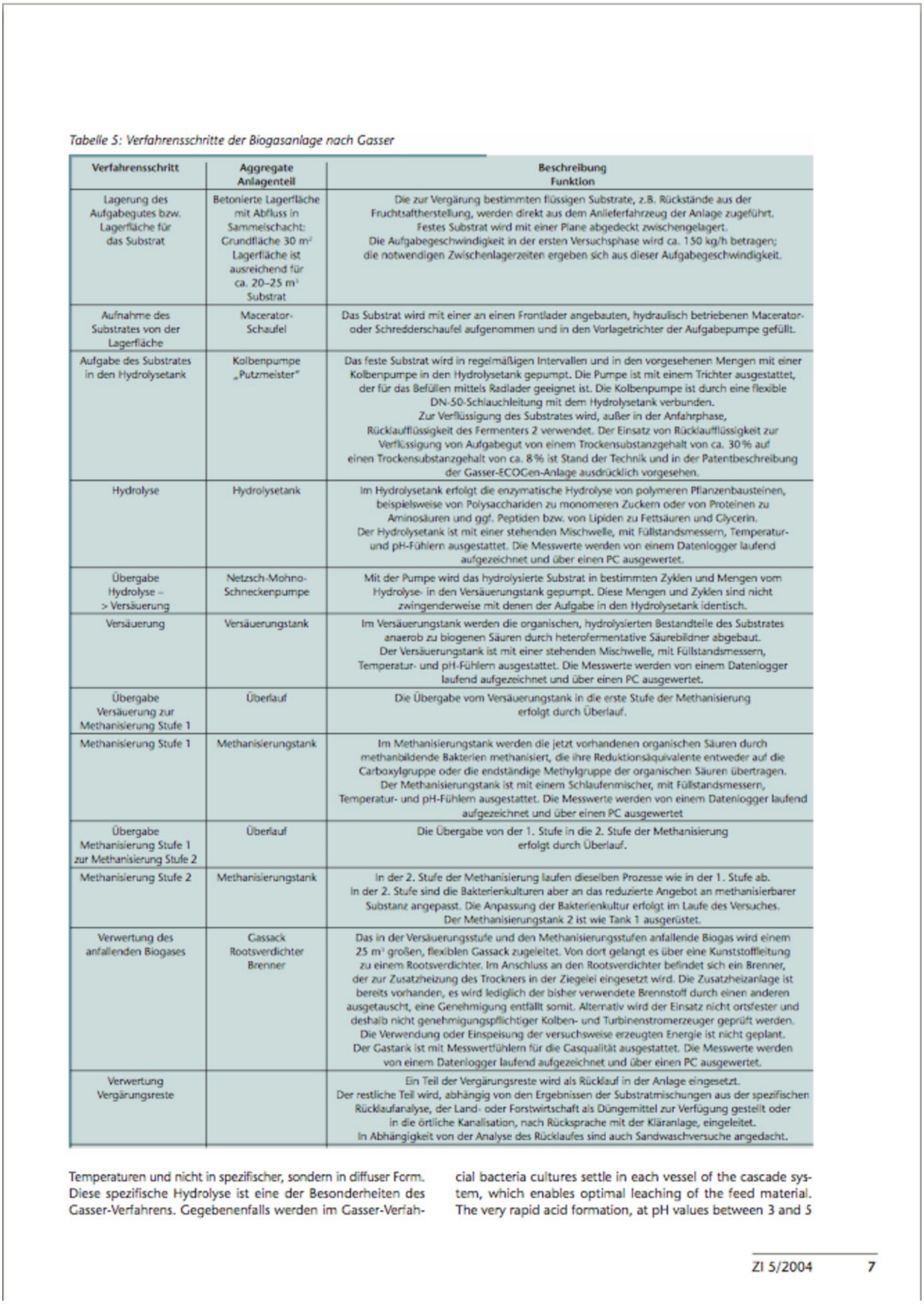


Tabelle 5: Verfahrensschritte der Biogasanlage nach Gasser

Verfahrensschritt	Aggregate Anlagenteil	Beschreibung Funktion
Lagerung des Aufgabegutes bzw. Lagerfläche für das Substrat	Betonierte Lagerfläche mit Abfluss in Sammelschacht: Grundfläche 30 m² Lagerfläche ist ausreichend für ca. 20–25 m³ Substrat	Die zur Vergärung bestimmten flüssigen Substrate, z.B. Rückstände aus der Fruchtsaftherstellung, werden direkt aus dem Anlieferfahrzeug der Anlage zugeführt. Festes Substrat wird mit einer Plane abgedeckt zwischengelagert. Die Aufgabegeschwindigkeit in der ersten Versuchsphase wird ca. 150 kg/h betragen; die notwendigen Zwischenlagerzeiten ergeben sich aus dieser Aufgabegeschwindigkeit.
Aufnahme des Substrates von der Lagerfläche	Macerator-Schaufel	Das Substrat wird mit einer an einen Frontlader angebauten, hydraulisch betriebenen Macerator- oder Schredderschaufel aufgenommen und in den Vorlagetrichter der Aufgabepumpe gefüllt.
Aufgabe des Substrates in den Hydrolysetank	Kolbenpumpe „Putzmeister"	Das feste Substrat wird in regelmäßigen Intervallen und in den vorgesehenen Mengen mit einer Kolbenpumpe in den Hydrolysetank gepumpt. Die Pumpe ist mit einem Trichter ausgestattet, der für das Befüllen mittels Radlader geeignet ist. Die Kolbenpumpe ist durch eine flexible DN-50-Schlauchleitung mit dem Hydrolysetank verbunden. Zur Verflüssigung des Substrates wird, außer in der Anfahrphase, Rücklaufflüssigkeit des Fermenters 2 verwendet. Der Einsatz von Rücklaufflüssigkeit zur Verflüssigung von Aufgabegut von einem Trockensubstanzgehalt von ca. 30 % auf einen Trockensubstanzgehalt von ca. 8 % ist Stand der Technik und in der Patentbeschreibung der Gasser-ECOGen-Anlage ausdrücklich vorgesehen.
Hydrolyse	Hydrolysetank	Im Hydrolysetank erfolgt die enzymatische Hydrolyse von polymeren Pflanzenbausteinen, beispielsweise von Polysacchariden zu monomeren Zuckern oder von Proteinen zu Aminosäuren und ggf. Peptiden bzw. von Lipiden zu Fettsäuren und Glycerin. Der Hydrolysetank ist mit einer stehenden Mischwelle, mit Füllstandsmessern, Temperatur- und pH-Fühlern ausgestattet. Die Messwerte werden von einem Datenlogger laufend aufgezeichnet und über einen PC ausgewertet.
Übergabe Hydrolyse –> Versäuerung	Netzsch-Mohno-Schneckenpumpe	Mit der Pumpe wird das hydrolysierte Substrat in bestimmten Zyklen und Mengen vom Hydrolyse- in den Versäuerungstank gepumpt. Diese Mengen und Zyklen sind nicht zwingenderweise mit denen der Aufgabe in den Hydrolysetank identisch.
Versäuerung	Versäuerungstank	Im Versäuerungstank werden die organischen, hydrolysierten Bestandteile des Substrates anaerob zu biogenen Säuren durch heterofermentative Säurebildner abgebaut. Der Versäuerungstank ist mit einer stehenden Mischwelle, mit Füllstandsmessern, Temperatur- und pH-Fühlern ausgestattet. Die Messwerte werden von einem Datenlogger laufend aufgezeichnet und über einen PC ausgewertet.
Übergabe Versäuerung zur Methanisierung Stufe 1	Überlauf	Die Übergabe vom Versäuerungstank in die erste Stufe der Methanisierung erfolgt durch Überlauf.
Methanisierung Stufe 1	Methanisierungstank	Im Methanisierungstank werden die jetzt vorhandenen organischen Säuren durch methanbildende Bakterien methanisiert, die ihre Reduktionsäquivalente entweder auf die Carboxylgruppe oder die endständige Methylgruppe der organischen Säuren übertragen. Der Methanisierungstank ist mit einem Schlaufenmischer, mit Füllstandsmessern, Temperatur- und pH-Fühlern ausgestattet. Die Messwerte werden von einem Datenlogger laufend aufgezeichnet und über einen PC ausgewertet
Übergabe Methanisierung Stufe 1 zur Methanisierung Stufe 2	Überlauf	Die Übergabe von der 1. Stufe in die 2. Stufe der Methanisierung erfolgt durch Überlauf.
Methanisierung Stufe 2	Methanisierungstank	In der 2. Stufe der Methanisierung laufen dieselben Prozesse wie in der 1. Stufe ab. In der 2. Stufe sind die Bakterienkulturen aber an das reduzierte Angebot an methanisierbarer Substanz angepasst. Die Anpassung der Bakterienkultur erfolgt im Laufe des Versuches. Der Methanisierungstank 2 ist wie Tank 1 ausgerüstet.
Verwertung des anfallenden Biogases	Gassack Rootsverdichter Brenner	Das in der Versäuerungsstufe und den Methanisierungsstufen anfallende Biogas wird einem 25 m³ großen, flexiblen Gassack zugeleitet. Von dort gelangt es über eine Kunststoffleitung zu einem Rootsverdichter. Im Anschluss an den Rootsverdichter befindet sich ein Brenner, der zur Zusatzheizung des Trockners in der Ziegelei eingesetzt wird. Die Zusatzheizanlage ist bereits vorhanden, es wird lediglich der bisher verwendete Brennstoff durch einen anderen ausgetauscht, eine Genehmigung entfällt somit. Alternativ wird der Einsatz nicht ortsfester und deshalb nicht genehmigungspflichtiger Kolben- und Turbinenstromerzeuger geprüft werden. Die Verwendung oder Einspeisung der versuchsweise erzeugten Energie ist nicht geplant. Der Gastank ist mit Messwertfühlern für die Gasqualität ausgestattet. Die Messwerte werden von einem Datenlogger laufend aufgezeichnet und über einen PC ausgewertet.
Verwertung Vergärungsreste		Ein Teil der Vergärungsreste wird als Rücklauf in der Anlage eingesetzt. Der restliche Teil wird, abhängig von den Ergebnissen der Substratmischungen aus der spezifischen Rücklaufanalyse, der Land- oder Forstwirtschaft als Düngemittel zur Verfügung gestellt oder in die örtliche Kanalisation, nach Rücksprache mit der Kläranlage, eingeleitet. In Abhängigkeit von der Analyse des Rücklaufes sind auch Sandwaschversuche angedacht.

Temperaturen und nicht in spezifischer, sondern in diffuser Form. Diese spezifische Hydrolyse ist eine der Besonderheiten des Gasser-Verfahrens. Gegebenenfalls werden im Gasser-Verfah-

cial bacteria cultures settle in each vessel of the cascade system, which enables optimal leaching of the feed material. The very rapid acid formation, at pH values between 3 and 5

Table 5: Process stages of the Gasser biogas plant

Process stage	Equipment Plant section	Description Function
Storage of the feed material and storage area for the substrate	Concrete-surfaced storage area with drainage in storage shaft: base area 30 m² Storage area is sufficient for approx. 20–25 m³ substrate	The liquid substrate for fermentation, e.g. residue from the production of fruit juice, is fed directly from the delivery vehicle to the plant. Solid substrate is covered with tarpaulin and stored intermediately. The feed rate in the first test phase will be around 150 kg/h; the necessary intermediate storage periods are calculated on the basis of this feed rate.
Collection of the substrate from the storage area	Macerator bucket	The substrate is picked up with a hydraulically operated macerator or shredder bucket and placed into the feed hopper of the feed pump.
Feed of the substrate into the hydrolysis tank	"Putzmeister" piston pump	A piston pump supplies the solid substrate at regular intervals and at a defined delivery rate to the hydrolysis tank. The pump is equipped with a hopper suitable for filling with a wheel loader. The piston pump is connected with the hydrolysis tank by a flexible DN 50 hose line. Apart from in the start-up phase, liquid recirculated from Fermenter 2 is used to liquefy the substrate. The use of the recirculated liquid to liquefy the feed material from a dry substance content of approx. 30% to a dry substance content of approx. 8% is state of the art and stipulated expressly in the patent specification of the Gasser ECOGen plant.
Hydrolysis	Hydrolysis tank	In the hydrolysis tank, the enzymatic hydrolysis of polymer vegetable units takes place, e.g. from polysaccharides to monomer sugars or from proteins to amino acids and, in some cases, peptides or from lipids to fatty acids and glycerine. The hydrolysis tank is equipped with a vertical mixing shaft, fill level indicators, temperature and pH sensors. The measured values are recorded continuously by a data logger and evaluated on a PC.
Transfer from hydrolysis –> acidification	Netzsch-Mohno-worm pump	The pump is used to transfer the hydrolyzed substrate in defined cycles and at set rates from the hydrolysis to the acidification tank. These rates and cycles do not automatically have to be identical with those of the feed to the hydrolysis tank.
Acidification	Acidification tank	In the acidification tank, the organic, hydrolyzed constituents of the substrate are digested in an anaerobic process to biogenic acids by heterofermentative acid formers. The acidification tank is equipped with a vertical mixing shaft, fill level indicators, temperature and pH sensors. The measured values are recorded continuously by a data logger and evaluated on a PC.
Transfer acidification to methanation stage 1	Overflow	Transfer from the acidification tank to the first stage of methanation is based on an overflow.
Methanation stage 1	Methanation tank	In the methanation tank, the organic acids now present are methanated by methane-forming bacteria, which transfer their reduction equivalents either to the carboxyl group or the terminal methyl group of the organic acids. The methanation tank is equipped with a loop-type agitator, with fill level indicators, temperature and pH sensors. The measured values are recorded continuously by a data logger and evaluated on a PC.
Transfer from methanation stage 1 to methanation stage 2	Overflow	Transfer from the first stage to the second stage of methanation is based on an overflow.
Methanation stage 2	Methanation tank	In the second methanation stage, the same processes take place as in the first stage. In the second stage, however, the bacteria cultures are adapted to the reduced availability of methanable substance. The bacterial culture is adapted in the course of the test. Methanation tank 2 is equipped like tank 1.
Utilization of the biogas produced	Gas bag Roots-compressor Burner	The biogas produced in the acidification and methanation stages is fed to a 25-m³-large, flexible gas bag. From here it is transferred in a plastic pipe to a roots compressor. Downstream of the roots compressor is a burner that is used for additional heating of the dryer in the brickworks. The additional heating system is already installed, only the fuel previously used has been replaced by a different one, no special approval must be obtained therefore. Alternatively, the use of piston and turbine generators that are not stationary and not subject to approval is currently being considered. The utilization or feed of the generated energy into the power grid is not planned. The gas tank is equipped with measurement sensors to monitor the gas quality. The measured values are recorded continuously by a data logger and evaluated on a PC.
Utilization of the fermentation residue		Part of the fermentation residue is returned for use in the plant. The remaining part is, depending on the results of the substrate mixtures from the specific return flow analysis, made available to agriculture or forestry as fertilizer or discharged into the local sewage system after consultation with the sewage treatment plant. Depending on the analysis of the return flow, even sand washing tests are planned.

ren dem Aufgabegut Enzyme oder ähnliche oder andere katalytisch wirkende Substanzen bei der Hydrolyse zugegeben; das kann auch Rückschlamm aus der Anlage sein.

Kaskadenfermentation

Im Anschluss an die Hydrolyse werden die zu fermentierenden Stoffe einer Versäuerung unter optimal definierten thermischen Bedingungen zugeführt.

and a temperature of around 40° C +/– 5° C, is performed in special fermenters. The acidified substrate is then fed in a low concentration to the downstream methanation fermenter.

Acidification forms the first stage in cascade fermentation, the methanogenic microorganisms being optimally adapted to the respective stages. The further digestion of the organic matter and methanation take place in a cascade of fermenters

Bei der Kaskadenversäuerung siedeln sich, ähnlich wie in einer Kläranlage, in jedem Behälter der Kaskade spezielle Bakterienkulturen an, was ein optimales Auslaugen des Aufgabegutes ermöglicht. Die sehr schnell ablaufende Säurebildung, bei pH-Werten zwischen 3 und 5 und einer Temperatur von ca. 40 °C +/– 5 °C, wird in eigenen Fermentern durchgeführt. Dann wird das gesäuerte Substrat in geringer Konzentration dem nachfolgenden Methanisierungs-Fermenter zudosiert.

Die Versäuerung bildet die erste Stufe der Kaskadenfermentation, wobei die methanogenen Mikroorganismen jeweils optimal der jeweiligen Stufe angepasst sind. Der weitere Abbau der organischen Substanz und die Methanisierung erfolgen in einer Kaskade von Fermentatoren, die mittels eines Zentralrohres und eines darin installierten Propellers homogen durchmischt werden (Schlaufenmischung).

In einer nachgeschalteten Stufe werden die Schwebeanteile im Fermentat mittels eines Hydrozyklones oder einer Zentrifuge entfernt. Die Reststoffe werden der Fermentation zugeführt oder als Porosierungsstoff bei der Herstellung von Wärmedämmziegeln eingesetzt.

Fazit

Das Gasser-Verfahren weist gegenüber anderen Verfahren folgende Vorteile auf:

- Es können im Prinzip alle organischen Reststoffe ohne Probleme verarbeitet werden
- Im Gegensatz zu herkömmlichen Biogasanlagen besteht kein Abwasserproblem, da die organische Substanz im Verfahren vollständig abgebaut wird
- kompakte Bauweise der Anlage
- reduzierte Investitionskosten
- hohe Betriebssicherheit

Die Fermentationsversuche mit dieser Anlage werden im Oktober 2004 abgeschlossen sein.

Wirtschaftliche Aspekte des Einsatzes von Biogas

Die Wirtschaftlichkeit des Einsatzes von regenerativen Brennstoffen hängt wesentlich davon ab, ob man für das zur Vergärung vorgesehene Substrat vom Abgeber eine Zuzahlung erhält oder nicht. In der Regel kann davon ausgegangen werden, dass eine Zuzahlung oder zumindest eine kostenlose Anlieferung erfolgt.

Ein weiterer wichtiger Punkt ist, dass von Seiten der EU die Voraussetzungen für den Handel mit so genannten CO_2-Zertifikaten geschaffen wurden. Aktuell gibt es nur Schätzungen und Prognosen über die Preise, da sich diese über Angebot und Nachfrage bilden werden. Derzeit ist noch nicht absehbar, wie großzügig die einzelnen Staaten ihre Unternehmen mit Zertifikaten ausstatten werden. In der Rentabilätsrechnung wird ein Wert von 10 € angesetzt. Im Falle der Ziegelei Gasser bedeutet das Mehreinnahmen von mindestens 35 000 €. Bei höheren Zertifikatspreisen erhöhen sich selbstverständlich auch die Mehreinnahmen.

Die Investitionsrechnung für die Anlage der Ziegelei Gasser, mit der eine Leistung von ca. 300 m^3/h angestrebt wird, weist einen Endbetrag von ca. 2,75 Mio. € auf, einschließlich aller Nebenleistungen.

In Südtirol werden für Anlagen dieser Art von Seiten der Landesregierung Zuschüsse gewährt. Im Rechenbeispiel sind weder diese Zuschüsse noch die eventuelle Erzeugung von elektrischer Energie berücksichtigt. Gleicherweise ist ein Ertrag

that are homogeneously agitated by means of a ducted axial flow impeller.

Downstream of the fermenter, the suspended matter in the fermentate is removed by a hydrocyclone or a centrifuge. The residues are fed to the fermentation process or used as pore-forming agents in the production of thermal insulating bricks.

Conclusion

Compared to other processes, the Gasser method boasts the following advantages:

- in principle, all organic residues can be processed without any problem
- in contrast to conventional biogas plants, there is no waste water problem as the organic substances are completely digested in the process
- compact design of the plant
- reduced investment costs
- high operational reliability

The fermentation tests with this plant will be concluded in October 2004.

Bild 6: Die Behälter für die Kaskadenfermentation werden aufgebaut

Fig. 6: The vessels for cascade fermentation are assembled

Economic aspects of the utilization of biogas

The economic efficiency of the utilization of regenerative fuels depends essentially on whether the company is paid to accept the substrate intended for fermentation by the company wanting to dispose of it or not. It can be generally assumed that a payment is received or the substrate is at least delivered free of charge.

Another important point are the conditions for trade with the CO_2 certificates created by the EU. At present, only estimates and forecasts are available regarding the prices of these certificates as these will be governed by supply and demand. It is not currently possible to say how generously the individual states will issue companies with certificates. In the profitability estimate, a value of 10 € has been taken for the certificates. For Gasser Brickworks, that works out at an additional income of at least € 35 000. If the certificates are priced higher, naturally the additional revenue will also increase.

The investment analysis for the plant at Gasser Brickworks, which targets a capacity of around 300 m^3/h, shows a final amount of around € 2.75 mill. including all supplementary payments.

Rentabilitätsrechnung für die ersten drei Geschäftsjahre/Profitability estimate for the first three business years

		Baujahr/Year of construction				Betrieb	
		Menge Quantity	Mengeneinheit ME Unit of quantity unit	je ME per unit [€]	Σ [€]	Menge Quantity	ei qua
Umsatzerlöse/Gross receipts							
CO$_2$-Zertifikate CO$_2$ certificates	Der Handel mit CO$_2$-Zertifikaten ist Gegenstand der Gesetzgebung und wird ab Januar 2005 möglich sein. Trade with CO$_2$ certificates is subject to legislation and will be possible from January 2005.				0.00	3 500.00	
Annahme Produktionsreste Acceptance of production waste	Reste aus der Speiseöl-, Lebensmittel- und Fruchtsaftherstellung usw. Waste from the production of cooking oil, food production and fruit juice production, etc.	250.00	t	45.00	11 250.00	500.00	
Annahme Speisereste Acceptance of food waste	Aus Getrenntsammlung. Die Annahmegebühren wirken sich stark auf die Rentabilität der Anlage aus und liegen derzeit zwischen 45 und 150 €/t. Im Falle der Zeigelei Gasser sind die Annahmegebühren sehr niedrig, was jedoch durch eine 1/3-Förderung (verlorener Zuschuss) der autonomen Provinz Südtirol-Bozen kompensiert wird. In der Cash-Flow-Rechnung der Anlage wären deshalb die realen Investitionskosten um 1/3 zu kürzen, was wiederum einen positiven Einfluss hätte. Aus Vergleichsgründen wurde in der vorliegenden Rechnung darauf verzichtet. From separate collection. The acceptance payments have a significant influence on the profitability of the plant and currently range between 45 and 150 €/t. The acceptance charges at Gasser Brickworks are very low, which, however, a 1/3 non-repayable subsidy granted by the autonomous Province of Southern Tyrol Bolzano compensate for. In the cash flow calculation for the plant, the real investment costs would therefore have to be decreased by 1/3, which would have a positive effect. For the purpose of comparison, this was not included in the present calculation.	250.00	t	1.00	250.00	7 500.00	
-/- Waren-/Materialeinsatz -/- Goods/material input							
Rohstoffe Raw materials	Es wird davon ausgegangen, dass bestimmte Rohstoffe zur Vergärung benötigt und bezahlt bzw. Frachtkosten übernommen werden müssen. Das betrifft bei Gasser gewisse Obsttrester. It is assumed that certain raw materials are necessary for fermentation and must be paid for or freight charges must be borne. At Gasser, this applies to certain fruit residue.	3 500.00	t	15.00	52 500.00	4 000.00	
= Rohertrag/= Gross yield					**–41 000.00**		
-/- Personalkosten einschl. Nebenkosten -/- Labour costs	Der Personalaufwand für die Biogasanlage ist gering. Es wird davon ausgegangen, dass eine zusätzliche Person für den Betrieb benötigt wird, die anderen Arbeiten können vom Personal der Ziegelei mit erledigt werden. The labour requirement for the biogas plant incl. incl. is low. It is assumed that one additional operative is needed for its operation, other work can be performed by the other operatives at the brickworks.	13.00	Monate months	3 415.50	44 401.50	13.00	
-/- Energiekosten (Heizung, Strom, Wasser) -/- Energy costs (heating, elec., the form water)	Für den Betrieb der Anlage fallen Stromkosten an. Heizung wird in Form von Rauchgas- oder Ofenwärmerückgewinnung beigestellt. Wasser, Brauchwasser wird benötigt, wenn nicht ausreichend flüssige Reststoffe vorhanden sind, um die notwendige Konzentration in den Fermentern zu erreichen. Electricity costs are incurred for operation of the plant. Heating is supplied in of flue gas or recovered from the kiln. Water, that is process water, is required if there is not sufficient liquid waste to obtain the necessary concentration in the fermenters.	32 850.00	kwh	0.14	4 599.00	219 000.00	
-/- Abwassergebühren -/- Waste water charges	Kosten für die Entsorgung der flüssigenPhase der Fermentationsreste fallen an. Costs for the disposal of the liquid phase of the fermentation residue.	4 562.50	m^3	4.50	20 531.25	18 250.00	
-/- betriebliche Versicherung -/- Business insurance	Fallen im Rahmen der üblichen Betriebsversicherung an. Within the scope of standard business insurance.	1.00	Pauschal flat rate	10 000.00	10 000.00	1.00	
-/- sonstige Betriebskosten	Fallen im Rahmen der üblichen Ausgaben der Ziegelei an.	1.00	Pauschal	25 000.00	25 000.00	1.00	

jahr 1/1st year of operation			Betriebsjahr 2/2nd year of operation				Betriebsjahr 3/3rd year of operation			
Mengen- nheit ME Unit of ntity unit	je ME per unit [€]	Σ [€]	Menge Quantity	Mengen-einheit ME Unit of quantity unit	je ME per unit [€]	Σ [€]	Menge Quantity	Mengen-einheit ME Unit of quantity unit	je ME per unit [€]	Σ [€]
t	10.00	35 000.00	3 500.00	t	10.00	35 000.00	3 500.00	t	10.00	35 000.00
t	45.00	22 500.00	2 000.00	t	45.00	90 000.00	3 500.00	t	45.00	157 500.00
t	1.00	7 500.00	7 500.00	t	1.00	7 500.00	7 500.00	t	1.00	7 500.00
t	15.00	60 000.00	2 500.00	t	15.00	37 500.00	1 000.00	t	15.00	15 000.00
		5 000.00			**95 000.00**				**185 000.00**	
Monate months	3 517.97	45 733.55	13.00	Monate months	3 623.50	47 105.55	13.00	Monate months	3 732.21	48 518.72
kwh	0.14	30 660.00	219 000.00	kwh	0.14	30 660.00	219 000.00	kwh	0.14	30 660.00
m^3	4.50	82 125.00	18 250.00	m^3	4.50	82 125.00	18 250.00	m^3	4.50	82 125.00
Pauschal flat rate	10 000.00	10 000.00	1.00	Pauschal flat rate	10 000.00	10 000.00	1.00	Pauschal flat rate	10 000.00	10 000.00
Pauschal	25 000.00	25 000.00	1.00	Pauschal	25 000.00	25 000.00	1.00	Pauschal	25 000.00	25 000.00

		Baujahr/Year of construction				Betrieb	
		Menge Quantity	Mengeneinheit ME Unit of quantity unit	je ME per unit [€]	∑ [€]	Menge Quantity	ei qua
Umsatzerlöse/Gross receipts							
-/- Other operating costs	Within the scope of standard expenses of the brickworks.	1.00	flat rate	25 000.00	25 000.00	1.00	
-/- Gebühren und Beiträge -/- Charges and contributions	Fallen im Rahmen der üblichen Ausgaben der Ziegelei an. Within the scope of standard expenses of the brickworks.	1.00	Pauschal flat rate	5 000.00	5 000.00	1.00	
-/- Sonstige Verwaltungskosten -/- Other administrative costs	Fallen im Rahmen der üblichen Ausgaben der Ziegelei an. Within the scope of standard expenses of the . brickworks.	1.00	Pauschal flat rate	5 000.00	5 000.00	1.00	
-/- Abschreibungen (Afa) 5 Jahre -/- Depreciation allowance 5 years	Die geringe Abschreibungsdauer von 5 Jahren wude bewusst gewählt, um das Investitionsrisiko so gering wie möglich zu halten. Nach dem heutigen Wissensstand wird von einer Anlagenlebensdauer von mindestens 15 Jahren ausgegangen. The short period of depreciation of five years was chosen to minimize the investment risk. Based on current knowledge, a plant lifetime of at least 15 years can be assumed.	76 296.00	1.00	1.00	76 296.00	508 640.00	
-/- Wartungsaufwand -/- Maintenance costs			Pauschal flat rate				
-/- Fremdkapitalzinsen -/- Interest on borrowed capital	Es wird von einer Finanzierungsdauer gleich der Abschreibungszeit ausgegangen. It is assumed that the financing period is equal to the period of depreciation.	83 925.60	1.00	1.00	83 925.60		
= Gewinn vor Steuern/Pre-tax-profit					**–315 753.35**		
+ Abschreibungen/Depreciation		76 296.00	1.00	1.00	76 296.00	508 640.00	
= Cash-Flow					**–239 457.35**		

Der Wert des erzeugten Brennstoffes beträgt ca. 150 000 € jährlich, ist in der Rechnung jedoch nicht berücksichtigt.
The value of the fuel produced amounts to around € 150 000 per year – this is not taken into account on the calculation.

für das produzierte Biogas nicht eingerechnet, obwohl er eigentlich berücksichtigt werden müsste. Ein eventueller Verkauf elektrischer Energie während der Stillstandszeiten der Ziegelherstellung ist ebenso nicht berücksichtigt (Strom aus regenerativen Quellen erzielt in Italien eine sehr gute Vergütung und stellt eine interessante Einnahmequelle dar. Im Falle der Ziegelei Gasser ist von Einnahmen aus Stromverkauf von mehr als 200 000 €/Jahr auszugehen).

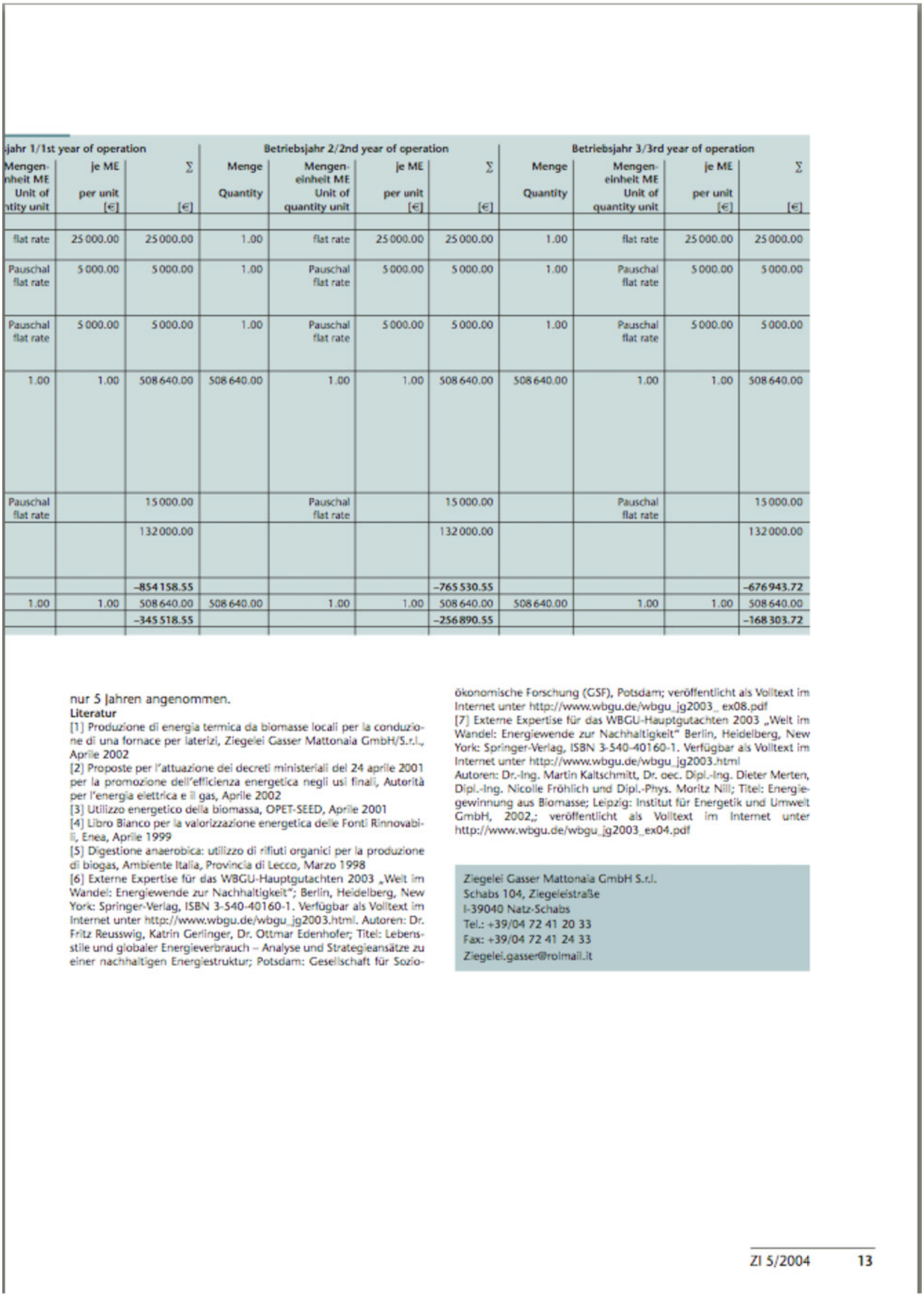
Einen ganz wesentlichen Einfluss auf die Wirtschaftlichkeit der Anlage haben die Kosten des Substrates. Wird ausschließlich Bioabfall als Substrat verwendet, erhöht sich die Wirtschaftlichkeit wesentlich.

Da bisher keine Erfahrungen mit dieser Anlage vorliegen, wurden die Amortisationszeit und die Rückzahlungszeit m

The regional government of the South Tyrol grants subsidies for plants of this type. Neither these subsidies nor the potential generation of electrical energy are taken into account in the example calculation. In the same way, revenue for the biogas produced is not included in the calculation either although this should really be taken into account. A possible sale of the electric energy during any stoppage in brick production is not taken into consideration either (power from regenerative sources sells at a good price in Italy and is an interesting source of revenue. In the case of Gasser Brickworks, revenue from the sale of electric power exceeding € 200 000 per year can be assumed).

The cost of the substrate is a very important factor influencing the economic efficiency of the plant. If biowaste is used exclusively as substrate, the economic efficiency of the process increases substantially.

Since no experience is available with the plant as yet, amortization and payback periods of just five years have been assumed.



jahr 1/1st year of operation			Betriebsjahr 2/2nd year of operation				Betriebsjahr 3/3rd year of operation			
Mengen-nheit ME Unit of ntity unit	je ME per unit [€]	Σ [€]	Menge Quantity	Mengen-einheit ME Unit of quantity unit	je ME per unit [€]	Σ [€]	Menge Quantity	Mengen-einheit ME Unit of quantity unit	je ME per unit [€]	Σ [€]
flat rate	25 000.00	25 000.00	1.00	flat rate	25 000.00	25 000.00	1.00	flat rate	25 000.00	25 000.00
Pauschal flat rate	5 000.00	5 000.00	1.00	Pauschal flat rate	5 000.00	5 000.00	1.00	Pauschal flat rate	5 000.00	5 000.00
Pauschal flat rate	5 000.00	5 000.00	1.00	Pauschal flat rate	5 000.00	5 000.00	1.00	Pauschal flat rate	5 000.00	5 000.00
1.00	1.00	508 640.00	508 640.00	1.00	1.00	508 640.00	508 640.00	1.00	1.00	508 640.00
Pauschal flat rate		15 000.00		Pauschal flat rate		15 000.00		Pauschal flat rate		15 000.00
		132 000.00				132 000.00				132 000.00
		–854 158.55				**–765 530.55**				**–676 943.72**
1.00	1.00	508 640.00	508 640.00	1.00	1.00	508 640.00	508 640.00	1.00	1.00	508 640.00
		–345 518.55				**–256 890.55**				**–168 303.72**

nur 5 Jahren angenommen.

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Converting a Large Scale Brick Operation to Renewable Fuels in a Developing Country

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Eng. Fritz Mödinger, formerly with Ziegel Gasser Mattoni (Italy), is now an independent contractor specialising in the conversion of brickyards to run on renewable energies. He is the holder of a patent for odour treatment of organic sludge, a patent for a cascade-type biogas plant.

Norbert Heidelmann (1962) graduated Dipl.-Ing./M. Eng. from RWTH Aachen, Germany. Key steps in his career were in the waste water and waste management sector and in renewable energy projects, climate change and carbon investments, and JI/CD management. He is at present with GreenStream Network GmbH (Germany).

Laura Lahti (1980) graduated in Environmental Planning from Turku University (Finland). Since 2007 she has been project manager at GreenStream Network GmbH (Germany) involved in the evaluation, development and management of climate protection projects under the Kyoto flexible mechanism.

Abstract

Tile & Brick International Manual 2008

A comprehensive overview of renewable and alternative fuels useable in brick production, including body fuels, is given and the gaseous emissions occurring during the drying and firing of hollow bricks in tunnel kilns are discussed.

The potential of the specific energy demand of a brick plant in Morocco is to be achieved through energy efficiency measures as part of an ongoing CDM (Clean Development Mechanism) project. Actual and expected emissions after both the energy efficiency measures and the fuel switch are presented.

Keywords: firing of bricks, alternative fuels, recycling of organic wastes, carbon dioxide emissions, sulphur, nitrogen oxide, volatile organic matter, dioxins, furans, chlorine, fluorine emissions, metals and metal compounds, energy saving potential, solid (petrol coke), liquid and gaseous fuels, conversion from fossil to alternative fuels

1 Introduction

The heavy clay industry can be roughly divided into three main branches:

- Roof tiles
- Facing bricks / pavers / pipes
- Structural bricks

While roof tiles and facing bricks rely exclusively on burners to generate a sufficient amount of heat to fire the products, structural bricks can also incorporate combustible substances, so called body fuels, within their body. These body fuels not only have the effect of generating thermal energy, they also modify the physical characteristics, reducing body density and hence improving the thermal insulation qualities of the product, i.e. of the brick manufactured.

The average energy consumption for the production of hollow bricks today can be estimated at 1,316 kJ/kg brick with the best values below 450 kJ/kg brick. Data are to be found in the following ranges (Table 1).

A comprehensive certainly not complete overview of renewable and alternative fuels useable in brick production, including body fuels, is given in Table 2.

Common to all solid fuels is that their combustion, if not used as a body fuel, is relatively awkward and not simple. In many cases chemical reactions between the solid fuel and the goods to be fired lead to unwanted, spotty changes in colour and, in the case of existing kilns, considerable modifications to the kiln body itself are mostly required to compensate the limited firing power of the single burner.

Recently, due to the high and rising cost of gas, solid fuels have been experiencing a certain revival in popularity. The problems associated with the use of solid fuels are manifold. These are, for example, corrosion of the kiln furniture and refractory linings, which have not been fully investigated yet. Emission problems – petrol coke for example can contain up to 12 % sulphur – are however limiting the use of solid fuels to some countries with less stringent environmental legislation or to plants with very efficient flue gas treatment systems.

During the firing and drying of the bricks, gaseous compounds are released either from the raw material fed, or the fuels used. Relevant emissions are:

- Sulphur dioxide and sulphur compounds that are closely related to the sulphur content of the raw materials and additives used themselves and the fuel employed. While natural gas is al-

Table 1 • Energy balance of tunnel kiln (data from own measurements and from literature)

Process	Energy requirement
Ceramic transformation	75–175 kJ/kg
Loss due to kiln car	110–300 kJ/kg
Flue gas loss	65–600 kJ/kg
Kiln insulation	10–190 kJ/kg
Cooling air	175–950 kJ/kg
Transformation of carbonates	15 kJ/kg carbonate content in % of total mass fired

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[2]) SBBC Societè Briqueterie Bati Chouia, Morocco

[1,3]) Greenstream Networks GmbH, Germany

Table 2 • Fuel types

Solid			Liquid			Gaseous		
Fossil	**Renewable**	**Alternative**	**Fossil**	**Renewable**	**Alternative**	**Fossil**	**Renewable**	**Alternative**
Petrol coke	Wood and similar	Combustible from household wastes	Light boiler oil	Vegetable oil and fat	Recycled frying fat	LNG	Biogas	Biogas
Anthracite		Combustible from industrial waste	Heavy boiler oil	Rendering fat	Motor oil Hydraulic oil	NG		Synthgas
Coke		Dried waste water treatment sludge cake		Bio diesel	Waste fatty acids			Landfill gas Sewage gas
Coal				Alcohol (methanol, ethanol)	Synthetic hydrocarbons			Hydrogen
					Pyrolysis oil			Pyrolysis gas

most free from sulphur, bio- or landfill gas can contain considerable amounts due to the bacterial conversion of proteins contained in the substrate. The raw material or waste used can contain sulphur in the form of pyrite (FeS_2), gypsum and other sulphates, and organic sulphur compounds. While sulphur is released into the environment, the reaction products are retained within the brick body.

- Nitrogen oxides and other nitrogen compounds are generated by "fixation" (an illustrative term used in the European BREF for the ceramic industry) of nitrogen and oxygen from the combustion air usually in the hot burner flames when the general kiln temperature is too low or at kiln temperatures above 1200 °C.
- Carbon monoxide, like carbon dioxide not associated with fuel firing, usually derives from organic matter contained in the clay body to be fired, especially under low oxygen firing conditions. The reaction of the carbon contained in the clay body with carbon dioxide, CO_2, released by the thermal dissociation of alkali and earth alkali carbonates such as calcium or magnesium during firing is another source of carbon monoxide and dioxide.
- Volatile organic compounds are released by organic matter contained in the clay itself or any form of additives. Carbonisation may occur with the release of complex and various VOCs.
- Dioxins and furans are usually not considered to be an issue in the brick industry. Nevertheless, measurements by Mödinger confirm their presence in the flue gas in measurable quantities even if the values, confirmed by measurements, are within the expected limits of about 0.1 ng TE/m³ [1]. In the presence of high chloride contents in the body, due to the clay itself or pore forming agents such as for example chloride bleached paper, this value could be exceeded. Dioxins are generally released from the combustion of carbon contained in the brick body in the normal production process of especially pored bricks in the temperature range of 250 °C to 350 °C in the preheating zone of the kiln whenever excess CO_2 is available [2]. To avoid the formation of dioxins and furans, a kiln design similar to the one used commonly today, illustrated in a later chapter, is most appropriate.
- Metals and metallic compounds are generally of limited concern, except if the fuel already contains such compounds. Tests at Gasser with a vegetable oil with a high zinc content have given empirical evidence of this.
- The emission of chlorine and chlorine compounds is due to the chlorine content in the clay itself, chlorinated mixing water, decomposition of chlorine rich mineral salts usually at temperatures >850 °C, and of organics in the temperature range 450 °C to 550 °C.

As with chlorine, the emission of fluorine is caused by fluorosilicates of various kinds present in the clay itself by decomposition at temperatures between 550 °C and 750 °C, depending on the mineral form, and by decomposition of CaF_2 at temperatures in excess of 900 °C.

Table 3 • Energy balance of tunnel kiln (data from[2] own measurements during improvement tests, and from literature[1])

Process	Energy requirement
[1] Process SBBC (potential)	1 144 kJ/kg brick (273.23 kcal/kg brick)
[2] Average brick industry	1 316 kJ/kg brick (314.33 kcal/kg brick)

Table 4 • Emission during and after brick firing with fossil fuel

Emissions foreseen gross without fuel switch					
Fuel (kiln + dryer)	35,77	8,93	43	74100	28.459,33
Petrolcoke	32,05	8,00	43	97500	33.546,70
Coke as body fuel	32,18	8,03	11,9	101000	9.656,20
		24,97			**71.662,23**
Emissions foreseen gross with fuel switch					
Fuel (kiln + dryer)	10,38	1,86	43	74100	5.915,18
Petrolcoke	44,72	8,00	43	97500	33.546,70
Coke as body fuel	44,90	8,03	11,9	101000	9.656,20
		17,89			**49.118,08**
					–22.544,15

Table 5 • Energy balance of tunnel kiln (data from own measurements and from literature)

Process	Energy requirement
GASSER process	1004 kJ/kg brick (240 kcal/kg brick)
Average brick industry	1316 kJ/kg brick (314.33 kcal/kg brick)

2 Benchmarking

Compared to installations used in the manufacture of hollow brick products in Europe and other parts of the world, the specific energy requirement of the SBBC Societé Briqueterie Bati Chaouia plant in Berrechid, Morocco, is higher than the corresponding common standards of the European brick industry as set out in Table 3.

The potential of the specific energy demand of the SBBC plant is to be achieved through energy efficiency measures as part of an ongoing CDM (Clean Development Mechanism) project. The higher the efficiency of the plant, the more successful its subsequent partial or total conversion to renewable fuels. In case of SBBC, the specific energy demand can be adjusted to almost 15 % below average benchmark standards. Considering that the plant runs partially on petrol coke – a fuel that in a tunnel kiln per se already commands high energy consumption due to increased losses – the result leads to a sustainable reduction of greenhouse emissions.

Apart from the energy efficiency measures, the conversion from fossil to alternative fuels at SBBC is a simultaneous ongoing venture also undertaken as a CDM project to generate additional required revenues from the sale of the CERs (Certified Emission Reductions) in order to overcome the investment hurdles. Actual and expected emissions after both the energy efficiency measures and the fuel switch are given in Table 4.

Fuels can be introduced in the brick making process in two ways:

- As "external" fuels – i.e. fuels combusted with the aid of a burner;
- As "internal" so-called body fuels – i.e. fuels mixed into the clay.

In both cases fuels can be either solid or liquid. Gaseous fuels can be used only as "external" fuels. Experience shows that "internal" body fuels, especially in densely set brick kilns, cannot exceed 20 % to 25 % of the total heat requirement of the process.

Another example is the Gasser brick works in Naz-Sciaves in the province of Bolzano, Italy, where the process has been adapted to run on renewable fuels, in this case solely fatty and recycled frying oil.

Compared to installations manufacturing hollow brick products in Europe, the specific energy requirement of the Gasser brick works, like SBBC, is well below the corresponding standards of the European brick industry (Table 5).

The higher the efficiency of the plant, the more successful is a partial or total conversion to renewable fuels. In the case of the Gasser brick works, the reduction in the energy demand resulted in almost 24 % compared to European benchmark standards.

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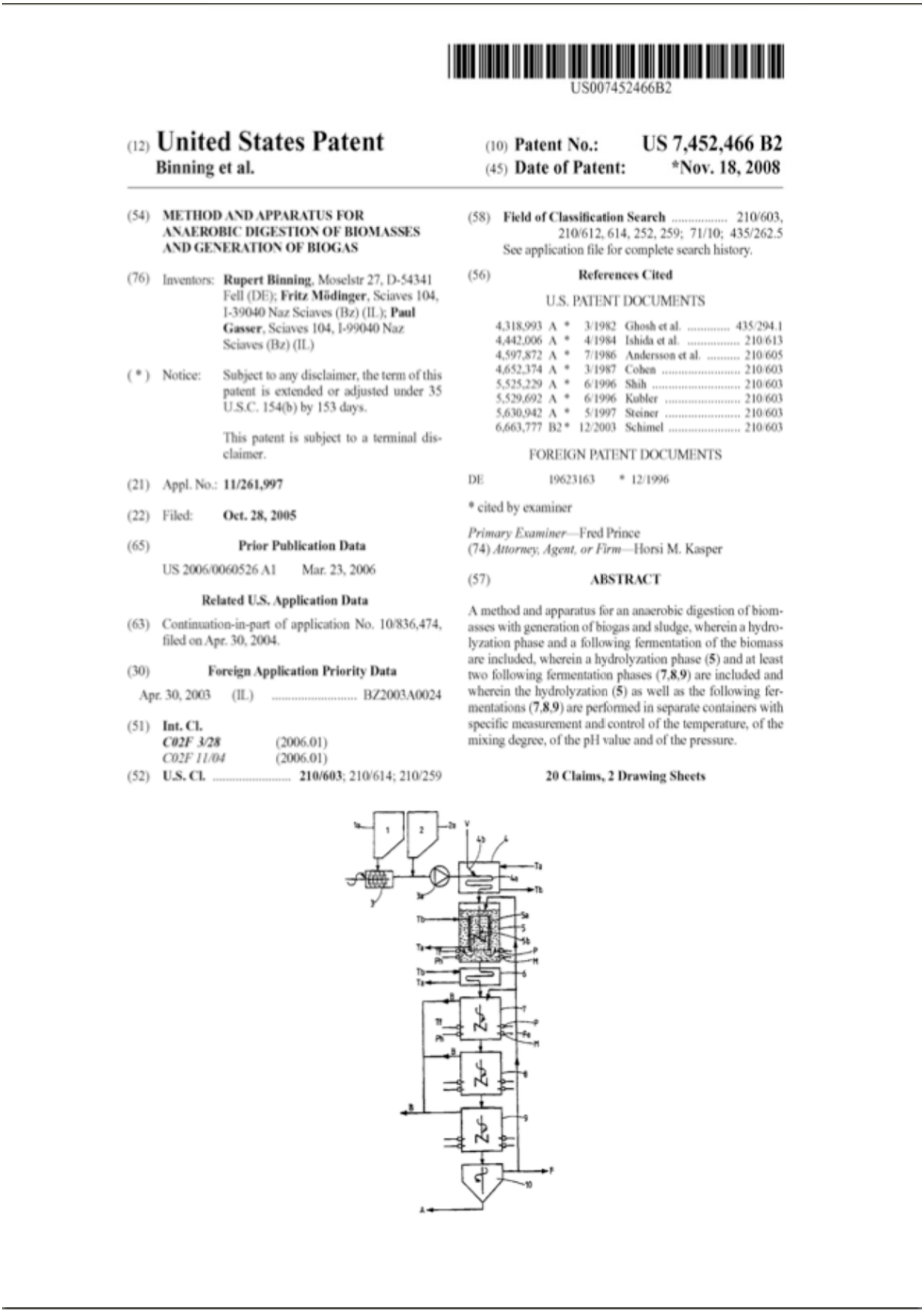

US007452466B2

(12) **United States Patent**
Binning et al.

(10) **Patent No.: US 7,452,466 B2**
(45) **Date of Patent: *Nov. 18, 2008**

(54) **METHOD AND APPARATUS FOR ANAEROBIC DIGESTION OF BIOMASSES AND GENERATION OF BIOGAS**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 153 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **11/261,997**

(22) Filed: **Oct. 28, 2005**

(65) **Prior Publication Data**

US 2006/0060526 A1 Mar. 23, 2006

Related U.S. Application Data

(63) Continuation-in-part of application No. 10/836,474, filed on Apr. 30, 2004.

(30) **Foreign Application Priority Data**

Apr. 30, 2003 (IL) BZ2003A0024

(51) **Int. Cl.**
C02F 3/28 (2006.01)
C02F 11/04 (2006.01)

(52) **U.S. Cl.** **210/603**; 210/614; 210/259

(58) **Field of Classification Search** 210/603, 210/612, 614, 252, 259; 71/10; 435/262.5
See application file for complete search history.

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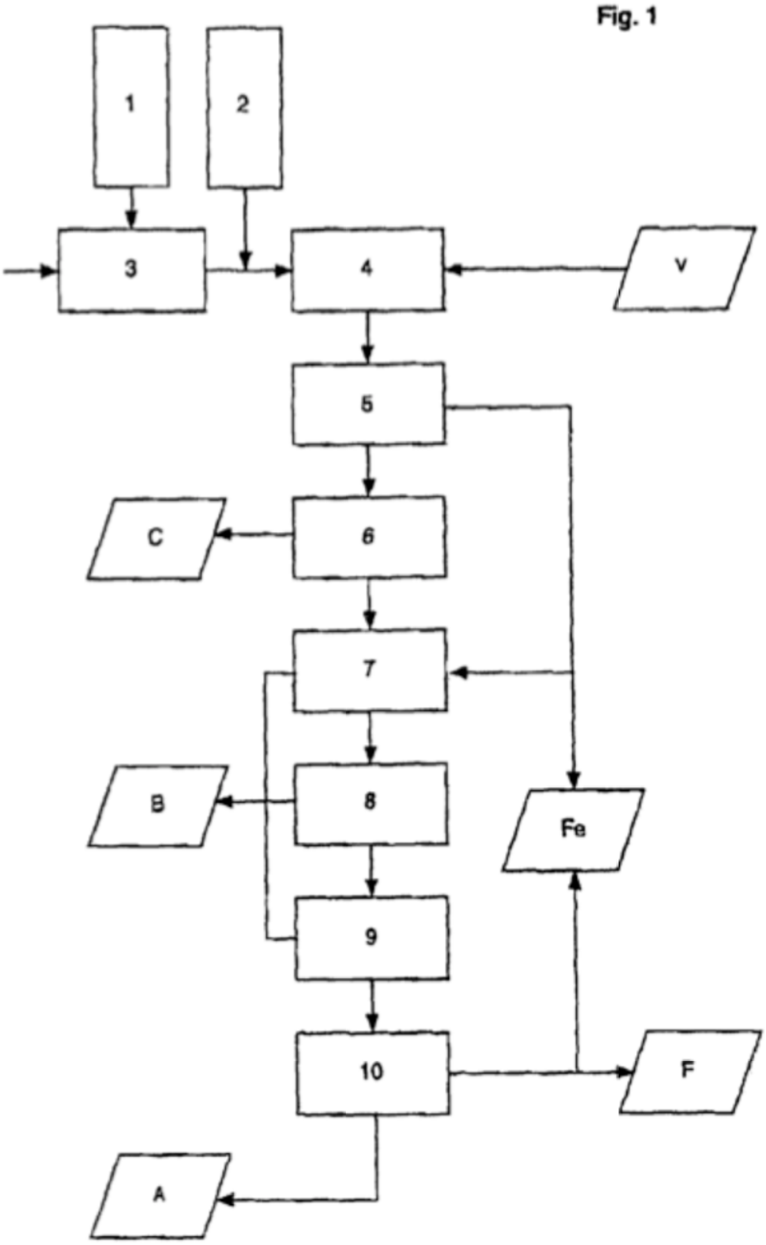
Primary Examiner—Fred Prince
(74) *Attorney, Agent, or Firm*—Horsi M. Kasper

(57) **ABSTRACT**

A method and apparatus for an anaerobic digestion of biomasses with generation of biogas and sludge, wherein a hydrolyzation phase and a following fermentation of the biomass are included, wherein a hydrolyzation phase (**5**) and at least two following fermentation phases (**7**,**8**,**9**) are included and wherein the hydrolyzation (**5**) as well as the following fermentations (**7**,**8**,**9**) are performed in separate containers with specific measurement and control of the temperature, of the mixing degree, of the pH value and of the pressure.

20 Claims, 2 Drawing Sheets

Fig. 1



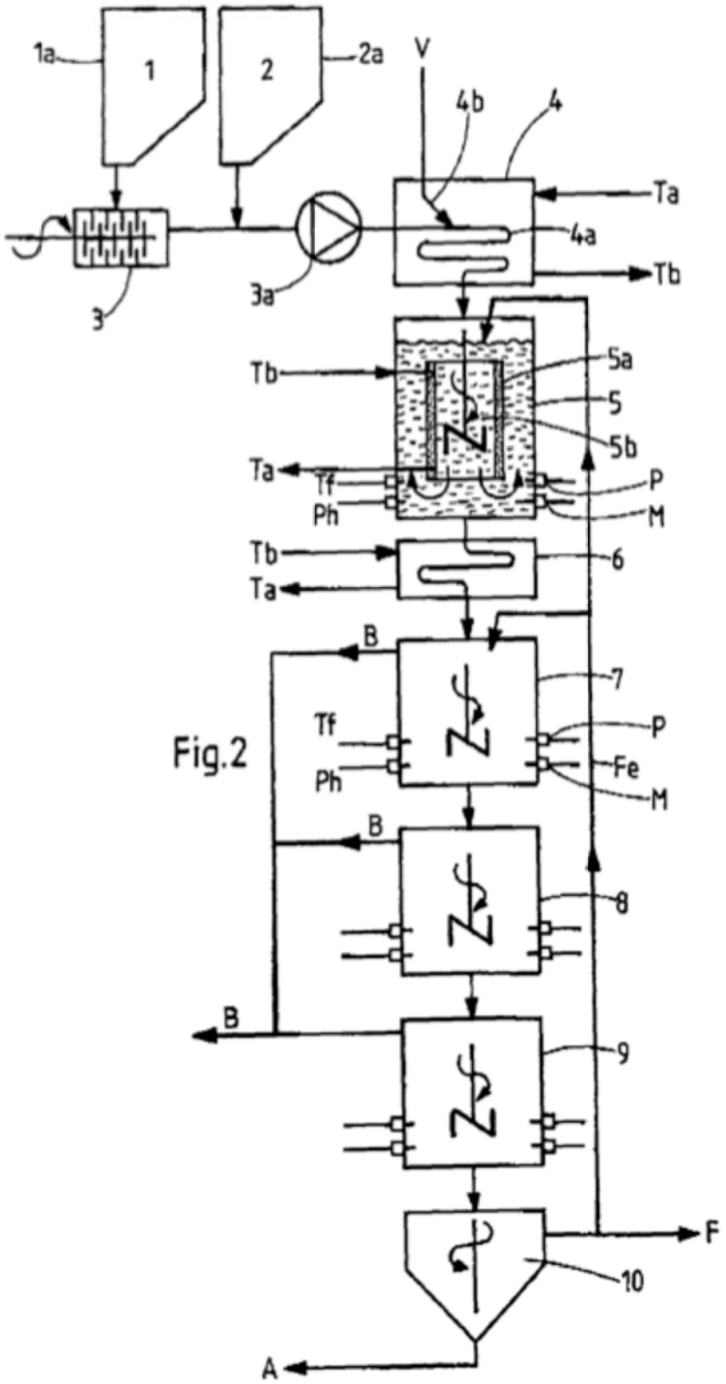


Fig.2

1a
1
2
2a
V
4b
4
Ta
4a
Tb
3
3a
Tb
5a
5
5b
Ta
Tf
Ph
P
M
Tb
Ta
6
B
7
Tf
Ph
P
Fe
M
B
8
B
9
F
10
A

METHOD AND APPARATUS FOR ANAEROBIC DIGESTION OF BIOMASSES AND GENERATION OF BIOGAS

RELATED APPLICATIONS

This application is a Continuation-in-part application of another application bearing Ser. No. 10/836,474 and filed on Apr. 30, 2004 and to be abandoned

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to a method and to an apparatus for anaerobic digestion of biomasses of different origin, consistency and chemical properties for the production of biogas.

2. Brief Description of the Background of the Invention Including Prior Art

Methods for the production of biogas with a fermenting machine or reactor are known, wherein complex organic materials (lipids, protids, glucids), which materials are contained in plants or in animal residual products, are destroyed and thereby enable to obtain energy by way of chemical reaction with the aid of enzymes, fungi and microorganisms, wherein these are formed in the biomass in the substrate of a biological origin (organic mass) under in each case defined process conditions. The fermentation is performed thanks to a non-aerobic flora of bacteria, which flora of bacteria is formed depending on the temperature prevailing in the fermentation machine. These bacteria are contained in the biomass and strongly multiply in a closed environment, wherein the enzymes serve as a catalyst; the enzymes react with the organic materials mostly to CH_4 (methane) and CO_2 (carbon dioxide).

The known methods and the plants for their realization do not take sufficiently into consideration that the non-aerobic flora of bacteria is formed of strains of bacteria, which strains of bacteria develop optimally at in each case specific temperatures between 25 degrees centigrade and 45 degrees centigrade and under specific environmental conditions. In addition there exists the risk that a too pronounced acidification occurs during the acidification phase caused by the formation of free acids and therefore the control of the pH value becomes difficult. This causes that the times, within which the individual process steps run, are becoming increased or, respectively, that the residues of the fermentation process are obtained which are not suitable for an advantageous employment of the process, since the residues contain not reacted or only partially reacted components. A too strong acidification can also cause the interruption of the biological course and therewith of the fermentation process. The precedingly recited methods and the corresponding apparatuses do not sufficiently take into consideration the influence of the temperature on the reaction and more generally those of the environmental situations under which the degradation reactions occur. In particular, the conditions for too high an acidification can occur during the phase of the acid formation. The too high formation of free acids and therewith difficult control of the pH values effects a slowing down of the course of the reaction and an incomplete conversion of the substrate with successive maintaining of residual products which are not suitable for later use because of the high content in organic materials.

SUMMARY OF THE INVENTION

1. Purposes of the Invention

It is an object of the present invention to realize a suitable method for the anaerobic digestion of biomasses of the above recited kind as well as a suitable apparatus for this purpose, by

way of which the conversion of the biomass is enabled, often the substrate of a biological origin (organic mass) for the purpose of processing biological waste of different origin, different particle size and consistency with different carbon to nitrogen C/N ratios and different humidity, with simultaneous optimation of the duration of the fermentation or, respectively, digestion process, with simultaneous increase of the degree of conversion of the methanogenous substrate, in order to obtain in this manner solid and liquid residues, which solid and liquid residues can be employed as a component in other production processes or in the same production process (recycling) or in different production cycles or in a recycling process.

It is a further object of the present invention to obtain the following advantages:

obtaining a higher yield of biogas,

obtaining solid and liquid residual volumes, which are suitable for the use as additives in production processes.

It is another object of the present invention to furnish a recovery process, where the reactions are performed under favorable conditions.

It is a further object of the invention to improve control of anaerobic digestion of biomasses.

These and other objects and advantages of the present invention will become evident from the description which follows.

2. Brief Description of the Invention

The present invention furnishes a method for achieving an improved anaerobic digestion of biomasses, wherein the method is subdivided as follows:

a specific pre-treatment of the diverse biomasses or of parts of the biomasses involving a mechanical comminution and/or a steam treatment and/or the heating to temperatures which effect a "hygienization" of the biomasses;

a cascade fermentation in order to create ideal conditions for the in each case specific requirements of the individual strands of the flora of the period in order to obtain in particular a methanization during several stages and separate from the acidification phase;

the feeding back of a part of the sludge, which sludge is produced in the last stage of the process, into the phases of hydrolysis and/or of fermentation with the purpose of feeding in of enzymes, which enzymes operate as biological catalysts;

the thickening of the sludge by way of a hydro cyclone through separation of residual liquids.

For resolving the object of the present invention there is disclosed a method, which is subdivided in the following way:

hydrolysis of the poly saccharides, of the proteins, of the lipids;

acidification under formation of simple biological acids;

single or multi-step methanization;

in order to obtain thereby an easier control of the pH value by separating the acidification step from the methanogenous step and by creating the in each case ideal conditions for the specific requirements of the individual bacteria strains of the anaerobic flora of bacteria by furnishing of a cascade fermentation.

The course of anaerobic digestion is performed essentially in three phases:

hydrolysis of the cellulose, of the sugars and of the amino acids;

acidic phase for forming of simple organic acids (for example acetic acid) and alcohols (for example ethyl alcohol);

methane formation by way of methanogenic bacteria through reaction of acids and alcohols into methane and carbon dioxide.

Hydrolysis, acidification, and methane generation

Hydrolysis, acidification, and methane generation have been described as biochemical processes, which have been realized on a large-scale. The present application does not teach many of the basic technical features of the individual underlying processes but is directed toward the spacial separation and the sequential performance of the processes in a cascade procedure.

Hydrolysis means that sugar, fats, and proteins are disintegrated into their basic building blocks. An important feature of the present method is the spacial separation of the hydrolysis based on the different compositions of the materials to be fermented. This is associated with the advantage that the bacteria, which are responsible for the hydrolysis of different starting materials, encounter in each case the best preconditions. Bacteria involved in sugar hydrolysis prefer a temperature of about 60 degrees centigrade. Bacteria involved in hydrolysis of proteins prefer a temperature of about 60 degrees centigrade. Bacteria associated with the hydrolysis of starches preferred temperatures around 90 degrees centigrade. Bacteria associated with the fat hydrolysis thrive best at an ambient temperature of 40 degrees centigrade. The coordinated separation of the processes depending on the starting material is a basic new feature of the present method.

The apparatus of the invention comprises:

a cutting plant for the comminution of the biomasses, which cutting plant is employed in particular for the biomasses with a carbon to nitrogen C/N ratio higher than 30 and a humidity content under 30 percent;

a fermentation machine which comprises separate and different reactors for the purpose of a more effective control of the reaction conditions of the individual process phases;

a heat treatment with the introduction of hot water vapor directly into the stream of the biomass and/or with a heat exchanger in order to obtain the "hygienization" of certain biomasses (for example starch containing biomasses);

a heat exchanger for bringing the temperature of the biomass at the discharge after the hydrolysation process to the ideal value for the following acidification process;

the obtained thermal energy can be used for pre-heating or for feeding thermal energy in one or in several process phases.

The different devices of the apparatus plant are equipped with thermal sensors and mixers in order to obtain the optimal thermal conditions for the in each case optimal effect of the specific strains of bacteria.

The novel features which are considered as characteristic for the invention are set forth in the appended claims.

The invention is illustrated by way of the accompanying drawings. The accompanying drawings represent schematically the course of the process according to the present invention or, respectively, the apparatus plant according to the present invention for an anaerobic digestion of biomasses of different origin, consistency, and chemical properties, for the generation of biogas, thickened sludge, and liquid residual materials. The invention itself, however, both as to its construction and its method of operation, together with additional objects and advantages thereof, will be best understood from the following description of specific embodiments when read in connection with the accompanying drawing.

BRIEF DESCRIPTION OF THE DRAWING

In the accompanying drawing, in which are shown several of the various possible embodiments of the present invention:

FIG. **1** is a view of a block diagram of the invention method.

FIG. **2** shows a block diagram of the apparatus and according to the present invention, wherein the apparatus plant operates according to the method presented in FIG. **1**.

DESCRIPTION OF INVENTION AND PREFERRED EMBODIMENT

The method of the Invention involves defining the major reactions of anaerobic digestion of biomass, substantially separating these steps by inducing a sequence of reaction steps, wherein the reaction steps furnish optimum conditions for sequentially performing the respective major reactions.

The method of the present invention generally comprises the following steps under defined conditions:

Comminuting a biomass,
Hydrolyzing the comminuted biomass,
Acidifying the hydrolyzed biomass
Generating methane in the acidified biomass.

A biomass is defined by originating from plants and animals. Examples of biomasses are carbon deposits, coals, oil deposits, oil shale, gas deposits, trees, composted leaves, waste discharges, food processing residues, paper residues, animal waste, fruits, grains, fish flour.

Comminuting is defined as reducing the grain size of the biomass.

The starting grain size of the processed biomass can be from about anything to 10 centimeters.

The grain size of the processed biomass after comminuting can be from about 0.1 to 10 millimeters and is preferably smaller than 1 millimeter.

Hydrolyzation is defined as splitting up of ether bonds or of ester bonds of organic materials of the biomass..

The comminuted biomass will contain a number of ether bonds per kilogram and hydrolyzation means that at least 70 percent by weight and preferably 90 percent by weight of the ether bonds become hydrolyzed.

The comminuted biomass will contain a number of ester bonds per kilogram and hydrolization means that at least 70 percent by weight and preferably 90 percent by weight of the ester bonds become hydrolyzed.

The hydrolyzed biomass will have a pH value in the range from pH 4 to pH 10.

The acidified biomass will have a pH value in the range of from pH 2 to pH 5.

The methane generation is defined as an anaerobic reaction of at least 50 molar percent of acetyl groups present in the acidified biomass to methane.

The method of the present invention will now be set forth in detail.

The biomass digestion process of the present invention is based upon the spatial separation of certain biological processes into separate phases.

A biomass mixture of **1**,**2** is taken from storage facilities or silos **1***a*, **2***a*, which contain bio waste **1** of the type of a large or coarse particle size with a carbon to nitrogen C/N ratio larger than about 30 and a humidity content under 30 percent and organic sludges **2** and/or biomasses of fine particle size with a molecular carbon to nitrogen C/N ratio advantageously below 30 and a content in humidity of advantageously above 30 percent. A coarse particle size has particle diameters up to 5 cm. A fine particle size has particle diameters from 0.1 mm to 1 mm and preferably not larger than 0.5 millimeters.

Conditions of cutting and comminuting

Cutting and comminuting refers to a purely mechanical process. The concepts aerobic and, respectively, anaerobic refer to reaction conditions which are performed in the presence of oxygen or, respectively, in the absence of oxygen. The chemical concepts of aerobic and anaerobic do not play a part in this context, since the cutting and comminution are independent of the chemical reaction conditions.

The charging volume of the starting biomass is fed to the cutting plant **3** for the purpose of comminuting into smaller particle sizes and is then fed to a pre-heater by way of a pump **3***a*, where the biomass is subjected to a heat addition (Ta-Tb) with the heat exchanger **4***a*. If required, water vapor V can employed for this purpose, wherein the water vapor can be injected in the charging region, in the discharging region of the heat exchanger, into the biomass or into the heat exchanger itself.

The water content of the comminuted biomass can be from about 40 to 80 weight percent and is preferably from 50 to 70 weight percent. The temperature of the comminuted biomass prior to hydrolysis can be from about ambient temperature to 100 degrees centigrade. The temperature of the comminuted biomass preferably is within 10 degrees of the temperature maintained in the following hydrolyzation tank. The above recited thermal treatments can be required for the hygienization of the biomass and/or for the thermal splitting of the starches. Usually the pre-heating in the biomass effects a temperature which doesn't surpass 100 degrees centigrade. Thereupon the biomass is fed to the hydrolyzer, which hydrolyzer as well as the following fermentation machines **7**,**8**,**9**, are equipped with a vertically standing double walled tube **5***a*, wherein a cooling agent (Tb-Ta) or, respectively, a thermal medium circulates inside the double walled tube **5***a* for controlling the temperature. In a first stage of the biomass digestion process the biomass is hydrolyzed, a chemical process in which a molecule is cleaved into two parts by the addition of a molecule of water and/or treated with enzymes as a catalyst. The used enzymes can be but are not limited to proteins and their complexes such as Oxidoreductases Transferases and/or Transferases and/or Hydrolases Transferases and/or Lyases Transferases and/or Isomerases Transferases and/or Ligases or any combination of the aforementioned. The hydrolysis enzymes are added to the comminuted biomass in an amount of from about 0.1. gram to 1 gram per kilogram of biomass. A separate addition of hydrolysis enzymes can be avoided in cases where it is possible to feed back reacted biomass containing hydrolysis enzymes.

In order to have sufficient amounts of corresponding bacteria present, the reaction containers can be associated with the respective fermentations storage, wherein the fermentation storage is connected to the input of the container and to the output of the container. The fermentation storage is fed from the output of the container containing substantial amounts of enzymes and bacteria, wherein the enzymes and bacteria are then re-entered into the container at the input side. This feature can be separately provided for the hydrolysis reactor, the acidification reactor, and/or the methane generating reactor.

The input of the hydrolysis reactor can contain materials which advance the hydrolysis in the hydrolysis reactor. These can be enzymes and bacteria which advance the hydrolysis reaction. This can be steam for adjusting the temperature during hydrolysis. This can be water for reducing the overall viscosity of the material subject to hydrolysis.

The anaerobic hydrolysis

All biochemical processes including the methane generation are anaerobic: during the hydrolysis, the biopolymers which are chemical compounds comprising chain or branch molecules, are disintegrated in their basic building blocks and other water-soluble decomposition products. It can be noted here that the fats are decomposed into fatty acids, that the carbohydrates such as for example poly saccharides are decomposed into mono or oligo saccharides and that the proteins such as albumin are decomposed into peptides or, respectively, amino acids. This reaction can be catalyzed as

desired by anaerobic microorganisms. As desired means here is that the biochemical reaction does not have to be performed in a complete absence of oxygen. Residual traces of oxygen do not necessarily impede the reaction. The hydrolysis bacteria perform the hydrolysis based on discharge of enzymes. This reaction step is the speed determining step based on the complexity of the starting materials.

The preferred reaction temperature for hydrolysis is to be found between 35° C. and 90° C. but can be, for specific biomasses, decreased or increased. The reaction time is usually to be found between 1 and 24 hours depending on the type of biomass.

Bacteria involved in sugar hydrolysis prefer a temperature of from about 50 to 70 degrees centigrade. Bacteria involved in hydrolysis of proteins prefer a temperature of from about 50 to 70 degrees centigrade. Bacteria associated with the hydrolysis of starches preferred temperatures from about 80 to 100 degrees centigrade. Bacteria associated with the fat hydrolysis thrive best at an ambient temperature of from about 30 to 50 degrees centigrade. The temperature of the hydrolysis container is set depending on the contents of the biomass in proteins, sugars, starches or fats. If different components (proteins, sugars, starches or fats) are simultaneously present in the biomass, then it can be advantageous to use two or three separate hydrolysis containers to be connected sequentially for providing an optimized and substantially complete hydrolyzation of the biomass. For example, a first hydrolysis container connected to the cutting apparatus operates at temperatures from about 30 to 50 degrees centigrade for hydrolyzing the fats, a second hydrolysis container sequentially connected to the first hydrolysis container operates at temperatures of from 50 to 70 degrees for hydrolyzing the sugars, and a third hydrolysis container connected to the acidifying container and sequentially connected to the second hydrolysis container operates at a temperature of from about 80 to 100 degrees centigrade for hydrolyzing the starches. Alternatively, the first hydrolysis container connected to the cutting apparatus operates at temperatures from about 80 to 100 degrees centigrade for hydrolyzing the starches, the second hydrolysis container sequentially connected to the first hydrolysis container operates at temperatures of from 50 to 70 degrees for hydrolyzing the sugars, and the third hydrolysis container connected to the acidifying container and sequentially connected to the second hydrolysis container operates at a temperature of from about 30 to 50 degrees centigrade for hydrolyzing the fats.

According to a preferred embodiment the hydrolysis reaction container can be provided as two or three sequential containers, wherein one container serves for the thriving of the fat hydrolysis bacteria at a temperature of about 40 degrees centigrade, wherein a second container serves for the thriving of the sugar hydrolysis bacteria and/or the protein hydrolysis bacteria at a temperature of about 60 degrees centigrade, and wherein a third container serves for the thriving of the starch hydrolysis bacteria at a temperature of about 90 degrees centigrade. Preferably the first container is for fat hydrolysis, the second container for sugar hydrolysis and protein hydrolysis, and the third container for starch hydrolysis.

The biomass needs to be mixed continuously during hydrolysis either by a compulsory mixing system with mixing paddles for example. In case of employing an internal mixer such as tube mixer with upwards or downwards flow direction, then a downwards flow is to be preferred in order to avoid the formation of sedimentary deposits at the bottom of the vessel. Mixing can be either continuously or intermittent whereas it has been shown that stopping mixing during the loading phase of the first vessel is advantageous.

The hydolysis is performed by operation of the respective enzymes in the hydrolysis reactor **5** preferably under specific surveillance and monitoring of the temperature with a temperature sensor (Tf), of the pressure with a pressure sensor (P), of the pH value with a pH-sensor (Ph), of the intermixing with an intermixing sensor (M) and of the gas discharge.

The hydrolysis according to the present invention takes place at temperatures between 40 degrees centigrade and 100 degrees centigrade in order to split the organic polymer substrates such as complex starches, pectin, hemicelluloses in the presence of and under interaction with hydrolysis enzymes (amylases, pectinases, hemicellulases), whereby predominantly mono saccharides and a substrate of low viscosity are formed, which substrate is thereby better available and better suited for the successive activity of the methanogenus bacteria.

The following steps are taken to control the reaction and to avoid that the hydrolysis is accompanied by acidification and/or methane formation.

Heat transferred to the biomass to be hydrolyzed with the aforementioned heat exchanger systems must be regulated in order to maintain the process temperature in the specific vessel at the desired temperature +/−5° C. Such regulation might be achieved by increasing or decreasing the flow of the heat exchanger medium by means of automatically controlled valves or by increasing or decreasing the temperature of the heat exchanger medium itself.

The hydrolysis stage is conventionally furnished for the generation of biogas. However a favorable generation of biogas occurs at substantially lower temperatures as compared with conventional hydrolysis temperatures. Conventionally, a hydrolysis reaction with biogas production occurs without a control of the temperature and of the intermixing depending on the properties and the concentration of biomass.

The hydrolysis is performed under anaerobic conditions.

In contrast, according to the present invention enzymes (amylases, pectinases, hemicellulases) or other materials such as for example several ferments can be added during the hydrolysis of the biomass, whereby eventually also a partially controlled feedback Fe of the sludges F is furnished, wherein the sludges F are taken out at the end of the course of the process.

Preferably, the following materials are added to the biomass during the hydrolysis stage: steam for controlling temperature and viscosity, hydrolysis enzymes and biomass feedback.

It is suitable to cool the hydrolyzed biomass substrate in a heat exchanger prior to feeding the hydrolyzed biomass substrate into the fermenting machines **7**,**8**,**9**, wherein possibly the heat is transferred to the cooling medium Tb-Ta, wherein then the cooling medium can be employed for the warming or pre-warming of the devices or of parts of the same plant or of a plant connected thereto.

The fermentation (acidification and methane generation) is performed like a cascade in separate fermenting machines **7**,**8**,**9** according to the present invention, wherein the separate fermenting machines **7**,**8**,**9** are in each case individually controllable and wherein specific cultures that directedly operate under optimum conditions relative to temperature, to intermixing, to the discharge of gas and to the pH value.

The optimum conditions are defined as follows:

It is known that the different anaerobic strains of bacteria develop their optimum activity of acidification in each case at different temperatures: the psicrophilous bacteria at temperatures below 15 degrees centigrade, the mesophilous bacteria at temperatures between 25 degrees centigrade and 45 degrees centigrade, and the thermophilous at temperatures above 45 degrees centigrade.

The formation of acids and/or the acidification by operation of the acid bacteria is performed in the first fermenting machine **7** always under specific surveillance and monitoring of the temperature with a temperature sensor (Tf), of the pressure with a pressure sensor (P), of the pH value with a pH-sensor (Ph), of the intermixing with an intermixing sensor (M) and of the gas discharge. The main culture strains are of the type *lactobacillus* (for example *lactobacillus casei, lactobacillus plantarum*) and of the type *streptococcus* (for example *streptococcus lactii, streptococcus cemoris*).

The input of the acidification reactor can contain materials which advance the acidification in the acidification reactor. These can be acidification bacteria and enzymes as well as pH controlling materials.

The anaerobic acidification

Like the hydrolysis, the acidification is as desired an anaerobic process. In the context of the acidification oxidation processes are running, however oxidation does not mean that free oxygen radicals have to be president. Oxygen containing compounds such as sulfate or nitrates are employed as electron acceptors instead of oxygen.

The fermentation for acidification

The acidification is performed in a common tank and at a pH value of from about 3 to 4. The electrical conductivity is small. After performing the acidification, the liquid containing acetic acid is led into the container where the methane generation is to take place.

The hydrolyzed biomass is then transferred into the acidification vessel by means of suitable pump such as a positive displacement pump or a centrifugal pump, with a constant or intermittent flow. It has been shown to be of advantage to interrupt mixing during acidification. It is preferred to transfer the hydrolyzed biomass from the bottom of the hydrolyzation vessel to the top of the acidification vessel. Acidification takes place at pH values in the range of 3 to 5 and at temperatures in the range of 25° C. to 65° C. Piping has to be dimensioned accordingly to the capacity of the pump, wherein flow speeds of 4 to 5 cm/sec are best suited for the purpose.

Following hydrolyzation and acidification, the preparatory process of the biomass, the acidified biomass is fed to the methane generators either by overflow from the acidification vessel or by a pump of the aforesaid type. In case of overflow this occurs whenever biomass is fed to the acidification vessel from the hydrolyzation vessel and hence the level in the acidification vessel reaches the point of overflow.

The proper methanogenus bacteria operate in the following fermenting machines **8**,**9**, wherein the methanogenus bacteria require the controlled feeding of bio genous acids in the acidified biomass substrate coming from the fermenting machine **7**. Mixed cultures, predominantly of the type the methanobacterium, methanosarcina, and methanococcus, operate in these fermenting machines. Cellulitis bacteria operate in symbiosis with the methanogenus bacteria, wherein the cellulitis bacteria effect the hydrolysis and the digestion of the organic materials with low solubility, such as for example cellulose.

Methane is produced by bacteria. The bacteria are anaerobes and operate only in anaerobic environments (no free oxygen). Constant temperature, pH and fresh organic matter promote maximum methane production.

The input of the methane generating reactor can contain materials which advance the methane generation in the methane generator. Such materials can be methane generating bacteria, acids or bases for controlling an appropriate pH value.

The anaerobic generation of methane

The methane generation is necessarily an anaerobic process, which means that no free oxygen radicals can be present in this process, since the catalytically acting bacteria do not have any protective mechanism against the oxygen radicals. This however does not exclude that the oxidation processes occur in connection with the methane generation. Oxygen containing compounds such as sulfate or nitrates are employed as electron acceptors instead of oxygen. Acetic acid generated during the acidification is transformed in the synthesis of methane by corresponding acetoclastic and acetic acid cracking formers of methane into methane and carbon dioxide as well as hydrogen.

Generation of methane

The generation of methane is preferably performed at the pH value of from about 7 to 8 and at a temperature of about 37 degrees centigrade.

Temperatures usually are maintained at from about 30 to 60 degrees centigrade and at approximately 40° C. during methane formation. Other temperatures can be used if held constant. For each 5° C. temperature decrease, gas production will be cut approximately one half or will take twice as long. A constant temperature is critical. Temperature variations of as little as 0,5° C. can inhibit the methane-formers enough to cause acid accumulation and possible digester failure.

The formation of methane by operation of the methanogenous bacteria is performed in the first and second biogas forming vessels **8**, **9** preferably under specific surveillance and monitoring of the temperature with a temperature sensor (Tf), of the pressure with a pressure sensor (P), of the pH value with a pH-sensor (Ph), of the intermixing with an intermixing sensor (M) and of the gas discharge.

The methane-formers break down the acids into methane and carbon dioxide. Since these anaerobic and methane forming bacteria multiply only very slowly, and since an anaerobic metabolism exhibits a small energy density, it is necessary to furnish a partial feedback Fe of the sludge F generated at the end of the process into the first phases of the fermentation **5**,**7**.

The methanogenus bacteria are present in nearly all materials, which are subject to an anaerobic disintegration (sewage sludge, moor sludge, swamp sludge, mining sludge) and are also present in the stomach of the ruminants in symbiosis, and for this reason the excrements of the ruminants are suitable as easily available starting cultures.

The separation of the reaction procedures

Important parameters are captured in the cutting plant **3**, namely the temperature, the electrical conductivity and the pH value. The temperature is a very important parameter and in contrast to simple chemical reactions the reaction speed is more complex in biochemical reactions depending on the temperature. The catalytical functioning of the bacteria influences to a large extent the reaction speed. This means in other words that the reaction runs at high speed if the preferred conditions of a defined stem of bacteria are created. The preferred reaction conditions for a stem of bacteria comprise the temperature, the pH value and the feeding material. Special reactions can be favored to occur and accelerated by a defined feeding material offerred and by a defined temperature. Then the hydrolysis is nearly concluded as determined for example by the conductivity measurements and the determination of pH value, then the material is pumped off and led into a storage container. The conditions in the storage container favor the fermentation and therefore run very quickly. It is of course a simplification if one says that a process runs only in one container containing such a slush, however the running of a single process is the case to a large extent and is based on the preferred treatment of one stem of bacteria with respect to feeding and preferred temperature, which very much influence in the multiplication speed of the bacteria.

The methane gas yield depending on the starting materials is shown in table 1.

The biogas B is withdrawn from each fermenting machine in a controlled fashion, which biogas B is possibly available as a renewable energy carrier. The completely disintegrated biomass substrate is led from the last fermenting machine **9** into a hydro cyclone **10**, wherein the separation of the residual liquid A is performed in the hydro cyclone **10**. These residual components are usable in different production cycles and in fact, for example as a porosity providing agent as it concerns the solid part, or as process water as it concerns the liquid part.

Spacial separation of reaction containers

The spacial separation of the individual phases of the process in different vessels and reactors permits an easier control of the pH value and reduces the risk of an over acidification by the formation of free acids. A further important characteristic value is the concentration of lignin. Since lignin is not decomposed in the process, the relative lignin content increases in the solid material residue. The parts of solid material at the beginning of the process that is after the cutting and comminuting, amounts to eight percent by weight. When the parts of solids have decreased to 0.5 percent, the assumption is proper that the residue is exclusively lignin. Consequently the process of gas generation is terminated. According to conventional plants the state is achieved after 30 to 40 hours. In contrast, plants according to the present invention reach the termination stage after about 15 hours.

The anaerobic digestion apparatus

The apparatus of the invention essentially comprises a sequence of vessels for sequentially performing the chemical and biological disintegration of the biomass.

A series of vessels joined by appropriate piping, valves and pumps such as illustrated later down are used to realize the anaerobic digestion apparatus.. The vessels, preferably silo type tanks, have a preferred but are not limited to a height/diameter relationship encompassed between 1:1 and 5:1. The vessels might be double walled or feature other means of obtaining extended surface heat transfer between the biomass substrate and a heating medium such as steam or heating oil maintaining a low differential temperature, <50° C., between the heat transfer surface and the biomass substrate.

The first storage container is connected with a first pipe to the cutting plant **3**. A third pipe connects the cutting plant **3** to a pump **3***a*. A second pipe connects the second storage container **2** to the third pipe and to the pump **3***a*. A fourth pipe connects the pump **3***a* to a pre-heater **4**. A fifth pipe connects the heat exchanger **4***a* to the hydrolysis container **5**, A sixth pipe connects the hydrolysis container **5** to a heat exchanger **6**. A seventh pipe connects the heat exchanger **6** to the acidification container **7**. An eighth pipe connects the acidification container **7** to a first biogas generator **8**. A ninth pipe connects the first biogas generator **8** to the second biogas generator **9**. A tenth pipe connects the second biogas generator to the hydro cyclone **10**. An eleventh pipe for feedback connects the hydro cyclone **10** to the acidification container **7**. A twelfth pipe for feedback connects the hydro cyclone **10** to the acidification container **5**.

The source of the bacteria and enzymes

The generation of methane is followed by an aerobic after clearing of the residue. The enzymes remain essentially intact during this process. A further important feature of the method is the back feed of the liquid which still contains bacteria and enzymes. The bacteria multiply the during optimal conditions very quickly and the still present enzymes also help starting the reactions. The spacial separation and the special treatment of the bacteria involved shows clearly how positive this point affects the overall process.

The charging volume of the starting biomass is fed from the storage containers **1**, **2** to the cutting plant **3** for the purpose of comminuting into smaller particle sizes and is then fed to a pre-heater **4** by way of a pump **3***a*, where the biomass is subjected to a heat addition (Ta—Tb) with the heat exchanger **4***a*. If required, water vapor V introduced by water vapor feed pipe **4***b* can be employed for this purpose, wherein the water vapor can be injected in the charging region or in the discharging region of the heat exchanger **4***a*, into the biomass or into the heat exchanger **4***a* itself.

The biomass is transported from the pre-heater **4** to the hydrolysis vessel **5**. The biomass needs to be mixed continuously during hydrolysis either by a compulsory mixing system, mixing paddles for example, or by any other suitable mixing device. Gas of a gas mixer **5***b* can be used to mix the biomass during hydrolysis. In the case of mixing paddles the flow speed when measured at the outer wall of the hydrolysis vessel shall be in the range of $2r\pi=0{,}25$ to $1{,}25$.

In case an internal mixer such as tube mixer is employed with upwards or downwards flow direction, then however a downwards flow direction is to be preferred in order to avoid the formation of sedimentary deposits at the bottom of the hydrolysis vessel.

The hydrolyzed biomass is then transferred through a heat exchanger **6** and the seventh pipe into the acidification vessel **7** by means of a suitable pump such as a positive displacement or centrifugal pump, with a constant or intermittent flow. It has been found to be of advantage to interrupt mixing during acidification. It is preferred to transfer the hydrolyzed biomass from the bottom of the hydrolysis vessel **5** to the top of the acidification vessel **7**. Acidification takes place at pH values in the range of 3 to 5 and at temperatures in the range of 25° C. to 65° C. Piping has to be dimensioned according to the capacity of the pump where flow speeds of 4 to 5 cm/sec are best suited for the purpose. Pumping with higher or lower flow speeds is nevertheless feasible and possible without any major detrimental effect on the process itself.

Following hydrolysis and acidification, the preparatory process of the biomass, the acidified biomass is fed to the methane generators **8**, **9** either by overflow from the acidification vessel **7** or by a pump of the aforesaid type. In case of overflow this occurs whenever biomass is fed to the acidification vessel **7** from the hydrolysis vessel and hence the level in the acidification vessel **7** reaches the point of overflow. An overflow can either be achieved in a bottom/top, top/top or top/bottom layout. A feed by overflow into the methane generating vessels **8**, **9** can only be achieved if the vessels are on the same level. In each other case a pump of the aforesaid type is to be used.

The hydrolysis vessel **5** as well as the following fermentation machines **7**,**8**,**9**, are equipped with a vertically standing double walled tube **5***a*, wherein a cooling agent (Tb—Ta) or, respectively, a thermal medium circulates inside the double walled tube **5***a* for controlling the temperature. Such regulation might be achieved by increasing or decreasing the flow of the heat exchanger medium by means of automatically controlled valves or by increasing or decreasing the temperature of the heat exchanger medium itself. Use of electric heating systems similar in type to water heaters is not recommended due to the build up of deposits on the outside of the heating elements when in contact with the biomass. Such regulation is best achieved by tying the temperature gauges installed on each vessel into a possibly automatically controlled system. An electromechanical system would be possible as well as due to the relatively large volumes of biomass contained in the vessels regulation is slow due to inertia of the masses.

A complete plant can feature one or more hydrolysis vessels and/or one or more acidification vessels.

Should one or more hydrolysis vessels and one or more acidification vessels be used with the same pump, appropriate valving has to be provided. If more than one acidification vessel **7** is associated with a specific hydrolyzation vessel **5**, then appropriate valving has to be installed. If a specified hydrolyzation vessel **5** is associated with a specific acidification vessel usually it is not necessary to provide valving as the pump will hinder backflow from the acidification vessel **7** into the hydrolysis vessel **5** at any time.

For both the hydrolysis and the acidification vessel, top, bottom or side mounted level gauges, temperature gauges and pH gauges are recommended in order to achieve optimal process data readings.

The vessels **8**, **9** used for methane generation can either be clustered, for example two or more vessels will form a cluster that in turn will represent a single stage in the multi stage methane generation process, to form a single vessel. Clustered vessels will have the advantage of lower building costs as standard components can be used. Single or clustered vessels will form a cascade. The clusters or single vessels will be connected between them in a way similar to the one described above.

Of course, all phases of the invention method provide for the recording of the data concerning temperature, pressure, flow speed, and chemical composition for the purpose of specific process control, which recording of data allows a high degree of effectiveness concerning the generation of biogas, of sludges F and of residual liquids A, which can be employed without problems in different production processes.

The invention method and the corresponding apparatus plant enable the processing of biomasses of very different origin, consistency and chemical properties, wherein the problems of discharging of liquid residual materials and of thickened sludges are resolved by the complete disintegration of the organic material and wherein the biogas generated, as well as the obtained heat are made useful for the operation of the plant itself or, respectively, as a renewable energy for example for the operation of plants of different kinds.

It will be understood that each of the elements described above, or two or more together, may also find a useful application in other types of waste recovery system configurations and biomass processing procedures differing from the types described above.

While the invention has been illustrated and described as embodied in the context of a method and apparatus for anaerobic digestion of biomasses and for generation of biogas, it is not intended to be limited to the details shown, since various modifications and structural changes may be made without departing in any way from the spirit of the present invention.

Without further analysis, the foregoing will so fully reveal the gist of the present invention that others can, by applying current knowledge, readily adapt it for various applications without omitting features that, from the standpoint of prior art, fairly constitute essential characteristics of the generic or specific aspects of this invention.

Summary Table of the Biogas Yield Depending on the Starting Materials

Biomass	m^3/k DS
Kitchen wastes	0.7-1.3
Biodegradeable packaging	0.64
Packaged food production wastes	0.32-0.8
Slaughterhouse wastes	0.34-0.71
Organic based oils and greases including lubricant oils	>0.5
Fishing wastes	~0.5
Differentiated waste collection	0.40-0.58
Potato wastes	~0.48
Wastes from the production of drugs	0.2-0.75
Potato distillation residues	~0.46
Beer production residues	0.42-0.5
Fruit distillation residues	0.45
Green waste	0.35-0.46
Sewage sludge	0.39-0.41
Manure	0.22-0.55
Paper and cardboard production wastes	0.2-0.3

What is claimed as new and desired to be protected by Letters Patent is set forth in the appended claims:

1. A method for an anaerobic digestion of biomasses with a generation of biogas and sludge comprising

fragmenting a biomass;

separately hydrolyzing the fragmented biomass;

separately acidifying the hydrolyzed biomass;

separately generating methane from the acidified biomass, wherein the hydrolyzing, the acidifying, and the generating of methane are performed successively on the biomass; and wherein the hydrolyzing, the acidifying, and the generating of methane are performed in separate containers under specific measurement and control of temperature, of intermixing, of a pH value and of a pressure.

2. The method according to claim **1** further comprising

pre-heating the biomass with a heat exchanger (**4***a*) and/or by way of injection of water vapor (V) prior to hydrolyzing,

wherein the hydrolyzing of the biomass is performed at a temperature between about 40 degrees centigrade and 100 degrees centigrade;

cooling the hydrolyzed biomass.

3. The method according to claim **2** further comprising

employing heat, which is led away during cooling (**6**), in one or in several phases (**4**,**5**,**7**,**8**,**9**) of the method or in another connected process for a pre-heating or heating.

4. The method according to claim **1** further comprising

feeding in of sludges (Fe) containing acid enzymes and produced at the end of the generating of methane under controlled conditions to the hydrolyzing of the biomass or to the acidifying of the biomass.

5. The method according to claim **1**, further comprising

performing the acidifying by acid forming enzymes;

wherein the generating of methane is furnished under a subjection with specific methanogenus bacteria, wherein the specific methanogenus bacteria are present in a container for generating biogas, wherein specific conditions relating to temperature, pH value, intermixing and pressure prevail in the container for generating biogas and performing fermenting.

6. The method according to claim **1** further comprising

thickening sludges (F) occurring at a discharge outlet of a last methane generating machine (**9**) in a hydro cyclone (**10**) or by way of a centrifuge;

separating a residual liquid (A) from solid residues.

7. The method according to claim **1** further comprising

withdrawing biogas (B) produced during the acidifying and the generating of methane under controlled conditions from each of individual fermentation machines.

8. A method for an anaerobic digestion of biomasses with a generation of biogas and sludge comprising

fragmenting a biomass;

separately hydrolyzing the fragmented biomass in a first reaction container;

measuring and controlling temperature, intermixing, pH-value and pressure in the first reaction container;

successively and separately acidifying the hydrolyzed biomass in a second reaction container;

measuring and controlling temperature, intermixing, pH-value and pressure in the second reaction container;

successively separately generating methane from the acidified biomass in a third reaction container,

measuring and controlling temperature, intermixing, pH-value and pressure in the third reaction container.

9. The method according to claim **8** further comprising

pre-heating the biomass with a heat exchanger (4a) and/or by way of injection of water vapor (V) prior to hydrolyzing,

wherein the hydrolyzing of the biomass is performed at a temperature between about 40 degrees centigrade and 100 degrees centigrade;

cooling the hydrolyzed biomass.

10. The method according to claim **9** further comprising

employing heat, which is led away during cooling (**6**), in one or in several phases (**4**,**5**,**7**,**8**,**9**) of the method or in another connected process for a pre-heating or heating.

11. The method according to claim **8** further comprising

feeding in of sludges (Fe) containing acid enzymes and produced at the end of the generating of methane under controlled conditions to the first container hydrolyzing the biomass or to the second container acidifying the biomass.

12. The method according to claim **8**, further comprising

performing the acidifying by acid forming enzymes;

wherein the generating of methane is furnished under a subjection with specific methanogenus bacteria, wherein the specific methanogenus bacteria are present in the third container for generating biogas, wherein specific conditions relating to temperature, pH value, intermixing and pressure prevail in the third container for generating biogas and performing fermenting.

13. The method according to claim **8** further comprising

thickening sludges (F) occurring at a discharge outlet of a last methane generating machine (**9**) in a hydro cyclone (**10**) or by way of a centrifuge;

separating a residual liquid (A) from solid residues.

14. The method according to claim **8** further comprising

withdrawing biogas (B) produced during the acidifying and the generating of methane under controlled conditions from each of individual fermentation machines.

15. An anaerobic decomposition apparatus comprising

a hydrolyzator (**5**) is furnished for an anaerobic digestion of a biomass substrate;

an acidifying vessel (**7**) connected to the hydrolyzator (**5**) in series;

a vessel for generating biogas (**8**) connected to the acidifying vessel and wherein, the hydrolyzator (**5**) as well as also the vessels are equipped with a heat exchanger (**4***a*), with mechanical, hydraulic, or gas mixers (**5***b*) and with sensors (Tf) or detectors for the determination of values relating to temperature, with sensors (Ph) or detectors for the determination of values relating to the pH value, with sensors (P) or detectors for the determination of values relating to the pressure, with sensors (M) or detectors for the determination of values relating to the degree of mixing, and wherein the heat exchanger (**4***a*), the gas mixer (**5***b*), the withdrawal of biogas and an introduction of fed back sludges (Fe) are operated depending on the recited determined values and of specific requirements of a flora of bacteria operating in the hydrolysator (**5**) and in the vessels (**7**,**8**,**9**).

16. The apparatus according to claim **15** further comprising

a preheater (**4**) disposed in front of the hydrolyzator (5) and furnished with a heat exchanger (**4***a*) and a device for the injection (**4***b*) of water vapor in a position ahead of the heat exchanger (**4***a*), after the heat exchanger (**4***a*), or in an intermediate position.

17. The apparatus according to claim **15** further comprising

a heat exchanger (**6**) furnished behind the hydrolyzator (**5**) for cooling of the hydrolyzed biomass substrate.

18. The apparatus according to claim **15** further comprising

an eleventh pipe connecting an output of the vessel for generating methane to the hydrolyzator for performing a controlled feedback (Fe) of sludges, which sludges are separated at the end of the apparatus; or

a twelfth pipe connecting an output of the vessel for generating methane to the acidifying vessel (**7**) for performing a controlled feedback (Fe) of sludges, which sludges are separated at the end of the apparatus.

19. An anaerobic decomposition apparatus comprising

a hydrolysis vessel (**5**) for an anaerobic digestion of a biomass substrate;

a first heat exchanger attached to the hydrolysis vessel;

a first mixer attached to the hydrolysis vessel;

a first detector (Tf) for detecting temperature in the hydrolysis vessel;

a first detector (Ph) for detecting a pH-value in the hydrolysis vessel;

a first detector (P) for detecting pressure in the hydrolysis vessel;

an acidifying vessel (**7**) connected to the hydrolysis vessel (**5**) in series;

a second heat exchanger attached to the acidifying vessel;

a second mixer attached to the acidifying vessel;

a second detector (Tf)for detecting temperature in the acidifying vessel;

a second detector (Ph) for detecting a pH-value in the acidifying vessel;

a second detector (P) for detecting pressure in the acidifying vessel;

a vessel for generating biogas (**8**) connected to the acidifying vessel;

a third heat exchanger attached to the vessel for generating biogas (**8**);

a third mixer attached to the vessel for generating biogas (**8**);

a third detector (Tf) for detecting temperature in the vessel for generating biogas (**8**);

a third detector (Ph) for detecting a pH-value in the vessel for generating biogas (**8**);

a third detector (P) for detecting pressure in the vessel for generating biogas (**8**).

20. The apparatus according to claim **19** further comprising

a first detector (M) for detecting a degree of mixing in the hydrolysis vessel;

a second detector (M) for detecting a degree of mixing in the acidifying vessel;

a third detector (M) for detecting a degree of mixing in the vessel for generating biogas;

a withdrawal port for withdrawing biogas and attached to the vessel for generating biogas;

a sixth pipe connecting the hydrolysis vessel (**5**) to the second heat exchanger (**6**); a seventh pipe connecting the second heat exchanger (**6**) to the acidifying vessel (**7**);

an eighth pipe connecting the acidifying vessel (**7**) to the vessel (**8**) for generating biogas;

a first feedback conduit connecting the vessel for generating biogas to the hydrolysis vessel;

a second feedback conduit connecting the vessel for generating biogas to the acidifying vessel; vessel;

and

wherein the first heat exchanger (**4***a*), the mixer (**5***b*), the withdrawal of biogas and an introduction of fed back-sludges (Fe) are operated depending on the detected values and of the specific requirements of the flora of bacteria operating in the hydrolysis vessel (**5**), in the acidifying vessel (**7**), and in the vessel (**8**,**9**) for generating biogas.

* * * * *

Appendix VII

A South Tyrolean Case Study: Mattoni Gasser Ziegel GmbH S.r.l.

Not published third party documents

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ITALIEN

Inhalt des Auftrages: Untersuchungen zur Charakterisierung von Ziegelrohstoffen ohne und mit Zusatzstoffen und zum Einfluss der Rohstoffzusammensetzung auf das Formgebungs-, Trocknungs- und Brennverhalten sowie auf die Produkteigenschaften

Probenahme: Auftraggeber

Probeneingang: 26.02. / 17.03. / 29.03.2009

<u>Zur Untersuchung lagen vor</u>:

Rohstoffproben

Ziegelrohstoff Vela Cortefranca (VC0)	K 3463
Ziegelrohstoff WB-Bubano (WBU0)	K 3465
Ziegelrohstoff WB-Bubano + 5 % Zusatz (WBU5)	K 3470
Ziegelrohstoff WB-Bubano + 15 % Zusatz (WBU15)	K 3471

Gliederung:

1. Vorbemerkung

Das Institut für Ziegelforschung wurde beauftragt, Untersuchungen zur Charakterisierung von Ziegelrohstoffen ohne und mit Zusatzstoffen und zum Einfluss der Rohstoffzusammensetzung auf die Produkteigenschaften durchzuführen.

Hierzu liegen zunächst zwei Ziegelrohstoffe ohne Zusätze vor, die laut Auftraggeber wie folgt bezeichnet sind:

Vela Cortefranca (VC0) und
WB-Bubano (WBU0).

Der Ziegelrohstoff WB-Bubano wurde zudem mit Zusatzstoffen in Zugabemengen von 5 und 15 % betriebsseitig versetzt, die als fertige Mischungen

WB-Bubano + 5 % Zusatz (WBU5) und
WB-Bubano + 15 % Zusatz (WBU15) vorliegen.

Für die nachfolgende Ergebnisdarstellung und Diskussion werden die Ziegelrohstoffe bzw. Mischungen mit den vom IZF gewählten und in den Klammern dargestellten Bezeichnungen verwendet.

Dem IZF liegen keine detaillierten Angaben über die Art und Zusammensetzung der Zusatzstoffe vor. An dieser Stelle sei schon darauf hingewiesen, dass die charakteristischen Kenndaten und Produkteigenschaften in keinem unmittelbaren Zusammenhang mit der Zugabemenge stehen. Hierauf wird im Verlauf der Ergebnisdarstellung noch genauer eingegangen. Die Berichterstattung setzt voraus, dass es sich bei den Mischungen WBU5 und WBU15 jeweils um den gleichen Zusatz handelt.

2. Rohstoffcharakteristik

2.1 Mineralanalyse (Tabelle 1)

Die Ermittlung der mineralogischen Zusammensetzung erfolgt röntgenographisch nach dem Zählrohrverfahren. Untersucht wird jeweils eine auf Analysenfeinheit nass gemahlene und bei 80 °C getrocknete, repräsentative Teilmenge der Originalprobe. Zur Feststellung quellfähiger Tonmineralkomponenten erfolgen zusätzliche Aufnahmen an scharf getrockneten sowie mit Aethylenglycol behandelten Probepräparaten. Der Quarzgehalt wird mit der Methode des „inneren Standards", der Karbonatgehalt nasschemisch bestimmt. Die Ergebnisse dieser Untersuchung sind in der Tabelle 1 wiedergegeben.

Ziegelrohstoff VC0

Der Ziegelrohstoff VC0 zeigt eine Vielzahl von Tonmineralen auf, die in Summe 48 Massen-% der Gesamtprobe ausmachen. Hierbei ist das Tonmineral Illit/Glimmer mit ca. 32 M.-% anteilsmäßig am stärksten vertreten. Die Tonminerale Illit-Smektit, Smektit und Chlorit liegen in vorgenannter Reihenfolge mit 3, 3 und 6 Massen-% vor. Der Kaolinit „Typ Fireclay" ist in einem Anteile von 4 Massen-% vertreten.

Neben den Tonmineralen sind die Tektosilikate mit 40 Massen-% und Karbonate mit 10 Massen-% aufgeführt. Die Tektosilikate beinhalten den „freien" Quarz mit 33 Massen-% und Albit und Kalifeldspat mit 5 bzw. 2 Massen-%. Die Feldspäte, die in ihrer Zusammensetzung mit denen der Tonminerale vergleichbar sind, liegen als unverwitterte Minerale vor. Die mit 10 Massen-% ausgewiesenen Karbonate setzen sich aus 9 % Calcit und 1 % Dolomit zusammen.

Massebezeichnung	VC0	WBU0	WBU5	WBU15
Rohstoff	K 3463	K 3465	K 3470	K 3471
Mineralart	Gesamtfraktion	Gesamtfraktion	Gesamtfraktion	Gesamtfraktion
Tonminerale:	**48**	**46**	**40**	**41**
Kaolinit (n)	n.n.	n.n.	n.n.	n.n.
Fireclay (n)	4	3	2	3
Illit / Glimmer (n)	32	29	24	24
Illit-Smektit (q)	3	3	4	4
Smektit (q)	3	3	3	3
Chlorit (n)	6	8	7	7
Chlorit-Vermikulit (q)	n.n.	n.n.	n.n.	n.n.
Tektosilikate:	**40**	**33**	**38**	**37**
Quarz	33	22	25	25
Albit	5	10	9	10
Kalifeldspat	2	1	4	2
Karbonate:	**10**	**20**	**21**	**18**
Calcit	9	17	16	15
Dolomit	1	3	5	3
Siderit	n.n.	n.n.	n.n.	n.n.
Oxide:	**< 1**	**n.n.**	**n.n.**	**< 1**
Hämatit	< 1	n.n.	n.n.	< 1
Anatas / Rutil	n.n. / n.n.	n.n. / n.n.	n.n. / n.n.	n.n. / n.n.
Hydroxide:	**1**	**< 1**	**< 1**	**< 1**
Goethit / Limonit	1 / n.n.	< 1 / n.n.	< 1 / n.n.	< 1 / n.n.
Lepidokrokit	n.n.	n.n.	n.n.	n.n.
Sulfide / Sulfate:	**n.n.**	**n.n.**	**n.n.**	**1**
Pyrit / Markasit	n.n. / n.n.	n.n. / n.n.	n.n. / n.n.	n.n. / n.n.
Gips / Jarosit	n.n. / n.n.	n.n. / n.n.	n.n. / n.n.	1 / n.n.
Sonstige:	**n.n.**	**n.n.**	**n.n.**	**n.n.**

Tabelle 1: Mineralanalyse von VC0, WBU0, WBU5 und WBU15

Ziegelrohstoff WBU0 – Mischungen WBU5 und WBU15

Der Tonmineralgehalt des Ziegelrohstoffes WBU0 liegt mit 46 Massen-% im Vergleich zu VC0 in ähnlicher Größenordnung, bei dem ebenfalls das Mineral Illit/Glimmer mit 29 Massen-% dominiert. Die Tektosilikate liegen in einem Anteil von 33 Massen-% vor. Den höchsten Anteil bildet mit 22 Massen-% der freie Quarz. Der Feldspat Albit ist mit

10 Massen-% vertreten. Die mit 20 Massen-% ausgewiesenen Karbonate setzen sich aus 17 % Calcit und 3 % Dolomit zusammen.
Durch die Zusätze wird innerhalb der Mischungen WBU5 und WBU15 der Tonmineralgehalt herabgesetzt und der Anteil an freiem Quarz erhöht. Unter der Voraussetzung, dass es sich jeweils um den gleichen Zusatzstoff handelt, müsste der Tonmineralgehalt den Zugabemengen entsprechend kontinuierlich abnehmen bzw. der Quarzgehalt zunehmen.

2.2 Chemische Analyse (Tabelle 2)

Die chemische Zusammensetzung wird durch röntgenfluoreszenzanalytische Aufnahmen (RFA) nach DIN 51001 bestimmt.

Elemente	VC0	WBU0	WBU5	WBU15
	K 3463	K 3465	K 3470	K 3471
Glühverlust	8.88	13.97	13.36	13.82
Silizium als SiO_2	60.59	49.21	52.05	50.11
Aluminium als	13.67	13.03	12.28	12.55
Titan als TiO_2	0.760	0.590	0.520	0.530
Eisen als Fe_2O_3	5.36	4.86	4.58	4.74
Kalzium als CaO	5.74	11.36	10.47	10.73
Magnesium als	1.73	3.05	2.83	3.02
Kalium als K_2O	2.12	2.28	2.19	2.15
Natrium als Na_2O	0.57	1.03	1.02	1.05
Mangan als	0.145	0.110	0.102	0.108
Barium als BaO	0.053	0.042	0.043	0.051
Vanadium als	0.018	0.018	0.017	0.015
Schwefel als SO_3	0.08	0.13	0.19	0.62
Summe	99.72	99.68	99.65	99.49

Tabelle 2: Chemische Vollanalyse von VC0, WBU0, WBU5 und WBU15

Ziegelrohstoff VC0

Das Siliziumoxid ist sowohl Bestandteil der Tonminerale als auch als freier Quarz vertreten. Der hohe Silizium-Gehalt von ca. 60 Massen-% korrespondiert mit dem, in der Mineralanalyse ausgewiesenen höheren Anteil an freiem Quarz. Aluminiumoxid ist mit 13,7 Massen-% vertreten. In Verbindung mit Siliziumoxid und unter Beteiligung der Alkali- und Erdalkalioxide sowie Metalloxide ergeben sich die in der Mineralanalyse ausgewiesenen unterschiedlichen Tonmineralarten. Der chemischen Analyse folgend, ist das Eisenoxid mit 5,4 Massen-% vertreten, das für die ziegelrote Brennfarbe verantwortlich ist. Das Kalzium- und Magnesiumoxid ist Bestandteil der Karbonate Calcit und Dolomit, die mit einer Aufhellung der Brennfarbe verbunden sind.

Ziegelrohstoff WBU0 – Mischungen WBU5 und WBU15

Aufgrund des vergleichsweise geringen Gehaltes an freiem Quarz ist das Siliziumoxid in einem gegenüber VC0 geringerem Anteil von ca. 49 Massen-% vertreten. Die Tonminerale bildenden Oxide, liegen im Vergleich zu VC0 in ähnlichen Anteilsmengen vor. Der höhere Anteil an Karbonaten spiegelt sich in den höheren Gehalten an Kalzium- und Magnesiumoxid wieder. Durch die Zusatzstoffe werden innerhalb der Mischungen WBU5 und WBU15 die Gehalte an Aluminiumoxid herabgesetzt und an Siliziumoxid erhöht. Diese Zu- bzw. Abnahme wird auch durch die in der Mineralanalyse ausgewiesenen Änderungen in den Tonmineralanteilen und Quarzgehalten bestätigt. Ein unmittelbarer Zusammenhang mit den Zugabemengen der Zusatzstoffe lässt sich aus den chemischen Analysen nicht ableiten.

Hinsichtlich der Gehalte an Fluor, Chlor sowie Sulfatschwefel und Pyritschwefel liegt dieser Berichterstattung der Prüfbericht Nr. CH 6811 bei.

2.3 Korngrößenanalyse (Tabelle 3)

Die Ermittlung der Korngrößenverteilung erfolgt mittels Siebanalyse. Dazu werden die im Anlieferungszustand vorliegenden Proben so vorbehandelt, dass ein Aufschluss der Bestandteile gegeben ist. Die Korngrößenfraktionen >0,045 mm (45 µm) Teilchendurchmesser wird mittels kombinierter Nass- und Trockensiebanalysen bestimmt, wobei zum Aufschluss Natriumpyrophosphat verwendet wird. Die Korngrößenfraktionen <45 µm Teilchendurchmesser werden mittels Sedigraph 5100 bestimmt. Die Nass- und die Trockensiebanalyse werden zur Kontrolle wiederholt. Die Mittelwerte der Ergebnisse sind zahlenmäßig in Anlage 3 aufgeführt.

Massebezeichnung	**VC0**	**WBU0**	**WBU5**	**WBU15**
Kornfraktion	**K 3463**	**K 3465**	**K 3470**	**K 3471**
> 4 mm	-	-	-	-
2,0 - 4,0 mm	0,2	< 0,1	0,2	0,1
1,0 - 2,0 mm	0,7	0,5	1,0	0,9
0,5 - 1,0 mm	1,0	0,7	3,4	2,6
0,25 - 0,5 mm	2,1	1,5	7,4	6,6
125 - 250 µm	4,7	4,0	11,6	9,6
63 - 125 µm	7,4	6,6	10,2	9,6
45 - 63 µm	3,3	2,7	3,4	3,0
20 - 45 µm	3,5	3,3	n.b.	n.b.
11,2 - 20 µm	6,2	6,5	n.b.	n.b.
6,4 - 11,2 µm	8,2	8,9	n.b.	n.b.
3,6 - 6,4 µm	9,3	9,5	n.b.	n.b.
2,0 - 3,6 µm	9,2	9,8	n.b.	n.b.
1,1 - 2,0 µm	9,5	9,8	n.b.	n.b.
< 1,1 µm	34,7	36,1	n.b.	n.b.
< 2 µm	44,2	45,9	n.b.	n.b.
2 - 20 µm	32,9	34,7	n.b.	n.b.
> 20 µm	22,9	19,4	n.b.	n.b.
	100,0	100,0	n.b.	n.b.

Tabelle 3: Korngrößenanalyse von VC0, WBU0, WBU5 und WBU15

Ziegelrohstoff VC0

Bei dem Ziegelrohstoff VC0 handelt es sich um ein insgesamt feinteiliges Material, dessen Kornfraktion <2 µm, der sogenannten Tonfraktion mit ca. 44 Massen-% belegt ist. Dieser für Hochlochziegelmassen recht hohe Anteil kann jedoch erst durch einen intensiven Aufschluss der zu messenden Substanz erreicht werden. Die Kornfraktion 2 – 20 µm ist mit 33 Massen-% belegt. Oberhalb von 20 µm ist ein Anteil von ca. 23 Massen-% vertreten. Der Grobkornanteil >1,0 mm von ca. 1 Massen-% besteht im Wesentlichen aus weißen splittrigem Korn. Einer chemischen Untersuchung entsprechend handelt es sich hierbei um Kalk- und Gipskörner.

Ziegelrohstoff WBU0 – Mischungen WBU5 und WBU15VC0

Der Ziegelrohstoff WBU0 ist ebenfalls als feinteiliges Material mit einem Anteil von ca. 46 Massen-% der Kornfraktion <2 µm, zu kennzeichnen. Diese Angabe entspricht dem Anteil der in der Mineralanalyse als Tonminerale ausgewiesen ist. Die gröberen Fraktionen >20 µm sind im Vergleich zu VC0 in geringeren Anteilen vertreten. Den vergleichsweise höheren Anteilen der Fraktionen 2 – 20 µm entsprechend, dürften die Karbonate Calcit und Dolomit in einer fein verteilten Form vorliegen.

Für die Mischungen WBU5 und WBU15 ist nur der Korngrößenbereich >45 µm ausgewiesen. Die innerhalb der Mischungen vorliegenden faserigen Leichtstoffe, sind im Zusammenhang mit dem Sedimentationsverfahren als Schwebstoffe anzusehen, die eine Messung der Kornfraktionen <45 µm verfälschen und dadurch ein unrealistisch hoher Anteil <2 µm ausgewiesen wird. Die Gegenüberstellung der Fraktionen >45 µm verdeutlichen jedoch, dass durch die Zusätze der Grobkornanteil maßgeblich erhöht wird. Der im Zusammenhang mit der Zugabemenge zu erwartende kontinuierliche Anstieg ist nicht gegeben.

Zusammenfassend ist festzustellen, dass die charakteristischen Kenndaten der Ziegelrohstoffe VC0 und WBU0 hinsichtlich der mineralogischen und chemischen Zusammensetzung sowie der Korngrößenverteilung denen entsprechen, die auch für eine Vielzahl von Ziegelrohstoffen ermittelt worden sind, die zur Herstellung von Hochlochziegeln eingesetzt werden. Wie eingangs schon erwähnt, liegen dem IZF keine genauen Angaben über die Art und Zusammensetzung der Zusätze vor. Prinzipiell ist der Zusatzstoff als magernde Komponente anzusehen, die den Tonmineralanteil herabsetzt und den Quarzgehalt erhöht. Hiermit ist auch eine Anhebung der Kornfraktion >63 µm verbunden. Der Fluorgehalt wird, bezogen auf den Ausgangsziegelrohstoff WBU0, nur geringfügig verändert. Die Gehalte an Chlor und Sulfat- sowie Pyritschwefel werden durch die Zusätze innerhalb der Mischungen erhöht. Insgesamt besteht jedoch eine Diskrepanz zwischen den charakteristischen Kenndaten und der Zugabemenge.

3. Keramtechnische Untersuchungen

Im Rahmen dieses Untersuchungsauftrages wird der Einfluss der Rohstoffzusammensetzung auf die Produkteigenschaften wie der Scherbenrohdichte, Biegezug- und Druckfestigkeit sowie der Scherben-Wärmeleitfähigkeit von Hochlochziegeln ermittelt.

3.1 Versuchsdurchführung

Massevorbereitung

Für die nachfolgenden Untersuchungen werden die Ziegelrohstoffe und Mischungen so eingesetzt, wie sie im Anlieferungszustand vorliegen. Zunächst wird der Anmachwassergehalt (Wasserbeladung) dahingehend korrigiert, dass die Steife des Massestranges einem Stauchwert von h_0/h_1 = ca. 1,67 (Messung nach Pfefferkorn, Reststauchhöhe 24 mm) entspricht.

Formgebung

Die Formgebung der vorbereiteten Mischungen VC0, WBU, WBU5 und WBU15 erfolgt auf einer Labor-Schneckenpresse mit Masseentlüftung (90 % Vakuum). Es werden Prüfziegel mit den Abmessungen 70 x 40 x 80 mm^3 (Lochanteil von 40 %) und Rundstäbe mit einem Durchmesser von 25 mm und einer Länge von 140 mm hergestellt. Die plattenförmigen Proben für die Bestimmung der Scherben-Wärmeleitfähigkeit haben die Abmessungen 110 x 40 x 300 mm^3.

Trocknung

Die Prüfziegel werden auf Drahtnetzen zunächst schonend in Raumluft und anschließend im Trockenschrank bei (105±5) °C getrocknet. Im Rahmen dieser Versuche werden die Anmachwassergehalte (Wasserbeladung) und die Trockenschwindungen bestimmt. Die Trockenbiegezugfestigkeit ist ein Maß für die Belastbarkeit der Ziegelrohlinge. Zudem erlaubt sie eine Aussage über den inneren Zusammenhalt der Masse, die auch Rückschlüsse auf das bildsame Verhalten zulassen. Zur Ermittlung der Trockenbiegezugfestigkeit werden getrocknete Rundstäbe – liegend auf zwei Schneiden – mit einem Abstand von 100 mm, mittig belastet. Die bis zum Bruch ermittelte Kraft wird auf das Widerstandsmoment des runden Querschnittes bezogen und als Biegezugfestigkeit ausgewiesen. Ergänzend zu diesen Untersuchungen wird der Test auf Trocknungsbruchanfälligkeit durchgeführt. Die Versuchsdurchführung und die Bewertungskriterien für die Trockenrissempfindlichkeit sind den Erläuterungen im Anhang zu entnehmen.

Brennen

Zur Charakterisierung des Ausdehnungs- und Schwindungsverhaltens während des Brennprozesses, wird die Längenänderung einer Probe mit einem Durchmesser von 6 mm und einer Länge von 27 mm - in Abhängigkeit von der Brenntemperatur – mit einem Dilatometer (Aufheizgeschwindigkeit von 10 K/min.) ermittelt.

Das Brennen der Prüfziegel erfolgt in einem gasbeheizten Kammerofen in oxydierender Atmosphäre (Sauerstoffgehalt von 12 bis 8 %) mit folgendem Aufheizprogramm:

100	–	700 °C	60 K/h
700	–	800 °C	12,5 K/h
ab		800 °C	40 K/h

Die Spitzentemperatur beträgt 850 und 920 °C, die Haltezeit jeweils 1 Stunde. Die verlangsamte Aufheizgeschwindigkeit im Temperaturbereich von 700 bis 800°C ist notwendig, um für die dickwandigen Platten zur Bestimmung der Scherben-Wärmeleitfähigkeit einen vollständigen Abbrand der organischen Bestandteile zu gewährleisten.

Im Rahmen dieser Versuche werden die Masseverluste, die Brennschwindungen und die Gesamtschwindungen bestimmt. Die Ermittlung des Erweichungsverhaltens im Garbrandtemperaturbereich, das die Höhe der in der Praxis maximal anwendbaren Spitzentemperatur wesentlich mitbestimmt, erfolgt an manuell geformten Biegestäbchen von 10 cm Länge. Diese werden im Ofen in waagerechter Position einseitig eingespannt, wobei sie mit 7 cm ihrer Länge frei über die Einspannvorrichtung hinausragen. Als Maß für die Erweichung wird die Umbiegung in mm unter Eigenlast ermittelt.

Für die Ermittlung der Neigung zur Reduktionskernbildung werden Rundstäbe von ca. 25 mm Durchmesser nach erfolgter Trocknung mit einer Temperatursteigerung von 120 K/h bis zu einer Spitzentemperatur von 900 °C in einem Kammerofen linear aufgeheizt und dann nach 5minütiger Haltezeit abgekühlt. Die zylindrischen Proben werden mittig getrennt, um im Falle eines unvollständigen Abbrandes die Größe der Reduktionskerne sichtbar zu machen. Die im Rahmen dieser Untersuchungen eingesetzten Ziegelrohstoffe und Mischungen zeigen bei den unter den vorgenannten Bedingungen gebrannten Proben keine Reduktionskerne. Selbst bei einer Aufheizgeschwindigkeit von 400 K/h treten nur geringe Kernverfärbungen auf.

Produkteigenschaften

Die Bestimmung der Wasseraufnahmefähigkeit der gebrannten Ziegel erfolgt durch 4-stündiges Kochen und anschließender 24-stündiger Wasserlagerung. Für die Ermittlung der Scherbenrohdichte werden die Rauminhalte der Prüfziegel nach dem Prinzip des Auftriebs von Körpern in Flüssigkeiten (Unterwasserwägung) bestimmt.

Um erste Anhaltspunkte bezüglich der voraussichtlich zu erwartenden Frostwiderstandsfähigkeit zu erhalten, wird der Tränkungswert (T-Wert) in Anlehnung an DIN 52251, Teil 3, bestimmt. Dieser Wert beschreibt den Anteil der unter Atmosphärendruck mit Wasser füllbaren, offenen Poren im Verhältnis zu den Poren, die sich bei Vakuum von 30 mbar mit Wasser füllen. Zur näheren Beurteilung dient die nachfolgende Tabelle.

Tränkungswert (T-Wert)		Beurteilung
bis	0,75	frostwiderstandsfähig
über	0,75 bis 0,85	bedingt frostwiderstandsfähig
über	0,85	frostgefährdet

Je kleiner der Tränkungswert ist, desto größer ist der für das gefrierende Wasser zur Verfügung stehende Ausdehnungsraum. So bedeutet ein Tränkungswert von 0,75 beispielsweise, dass beim Gefrieren des Wassers immerhin noch 25 % der offenen Poren als Ausdehnungsraum zu Verfügung stehen.

Der Test auf Ausblühung wurde durchgeführt, um erste Hinweise zu erhalten, ob eine Gefahr besteht, dass aus den Ziegelrohstoffen und Mischungen gefertigte Ziegel bei Feuchteeinwirkung zu Ausblühungen neigen. Hierzu wird ein gebrannter Prüfziegel aufrecht, bis zu etwa einem Drittel seiner Länge, in destilliertes Wasser gestellt und über einen Zeitraum von 14 Tagen darin belassen. Während dieser Zeit wird der Wasserspiegel durch Nachfüllen auf etwa gleicher Höhe gehalten. Nach Verdunsten sämtlichen Wassers wird der Prüfziegel bei 40 °C getrocknet, um an der Oberfläche abgelagerte Ausblühsalze deutlicher erkennen und optisch bewerten zu können.

Zur Ermittlung der Biegezugfestigkeit werden ebenfalls gebrannte Rundstäbe - liegend auf zwei Schneiden - mit einem Abstand von 100 mm, mittig belastet. Die bis zum Bruch ermittelte Kraft wird auf das Widerstandsmoment des runden Querschnitts bezogen und als Biegezugfestigkeit ausgewiesen.

Die Prüfung der Druckfestigkeit erfolgt in Strangrichtung der Prüfziegel. Hierfür werden die Druckflächen mit einem Zementmörtel planparallel abgeglichen. Im Hinblick auf die bei derartigen Prüfungen unvermeidbaren Messwertstreuungen werden je Massemischung mehrere Proben abgedrückt.

Die Bestimmung der Scherben-Wärmeleitfähigkeit erfolgt nach dem Heißdrahtverfahren (Kreuzstromanordnung) in Anlehnung an DIN 51046. Bei diesem einstationären Messverfahren wird der Temperaturanstieg einer im Probekörper befindlichen linienförmigen Wärmequelle in Form eines Heißdrahtes gemessen. Diesem Draht wird über die gesamte Messzeit eine konstante Leistung zugeführt. Das auf die Mitte des Heißdrahtes aufgeschweißte Thermoelement registriert den zeitlichen Temperaturanstieg, welcher ein Maß für den Wärmeleitkoeffizienten λ ist.

3.2 Einfluss der Massezusammensetzung auf das Formgebungs-, Trocknungs- und Brennverhalten sowie auf die Produkteigenschaften

Für die Zielsetzung dieses Auftrags stand die Ermittlung der Abhängigkeit der Produkteigenschaften von der Ziegelrohstoffzusammensetzung im Vordergrund. Die Ergebnisdarstellung befasst sich, neben dem keramtechnischen Verhalten, schwerpunktmäßig mit der Scherbenbildung insbesondere mit der Entwicklung der Scherbenrohdichte, Festigkeit und Scherben-Wärmeleitfähigkeit.

Formgebungs- und Trocknungsverhalten (Tabellen 4)

Ziegelrohstoff VC0

Zunächst ist festzustellen, dass sich die Mischungen unter Anwendung eines Vakuums von 90 % maschinell gut verpressen lassen.

Zur Erzielung einer Massesteife von 1,67 (Reststauchhöhe von 24 mm nach Pfefferkorn) ist eine Wasserbeladung von 23,4 Massen-% erforderlich. Durch die maschinelle Formgebung mit Vakuum erhöht sich die Massesteife auf einer Reststauchhöhe von 28 mm (Werte in Klammern). Bei kontinuierlichem Massefluss ergibt sich ein Presskopfdruck von 900 kPa. In Verbindung mit den Werten der linearen Trockenschwindung von 6,5 % und der Trockenbiegezugfestigkeit von 7,4 N/mm² ist der Ziegelrohstoff VC0 als bildsam zu beschreiben. Diese Eigenschaft wird durch den vergleichsweise hohen Tonmineralgehalt und die hohe Kornfeinheit vermittelt. Eine erhöhte Neigung zur Texturbildung ist nicht erkennbar. Die Trockenrissempfindlichkeit und Trocknungsbruchanfälligkeit ist als mäßig zu bewerten.

Massebezeichnung	VC0 K 3463	WBU0 K 3465	WBU5 K 3470	WBU15 K 3471
Massezusammensetzung	100 M.-%	100 M.-%	100 M.-%	100 M.-%
Formgebung	manuell (ohne Vakuum)			
Reststauchhöhe	24 (28)	24 (27)	24 (27)	24 (28)
Massesteife (nach Pfefferkorn)	1,67	1,67	1,67	1,67
Wasserbeladung (Anmachwasser)	23,4	24,9	23,6	24,3
lin. Trockenschwindung	6,5	7,3	6,9	6,8
Zeit bis zur ersten Rissbildung	8,6	6,8	8,7	8,9
Trockenrissempfindlichkeit	mäßig	erhöht	mäßig	mäßig
Tb-Wert	0,76	1,07	0,79	0,76
Trocknungsbruchanfälligkeit	mäßig	erhöht	mäßig	mäßig

Tabelle 4: Formgebungs- und Trocknungseigenschaften von VC0, WBU0, WBU5 und WBU15

Ziegelrohstoff WBU und Mischungen WBU5 und WBU15

Für den Ziegelrohstoff WBU ist zur Erzielung einer Massesteife von 1,67 (Reststauchhöhe von 24 mm nach Pfefferkorn) eine Wasserbeladung von 24,9 Massen-% erforderlich. Durch die maschinelle Formgebung mit Vakuum erhöht sich die Massesteife auf eine Reststauchhöhe von 27 mm (Werte in Klammern). Bei kontinuierlichem Massefluss ergibt sich ein Presskopfdruck von 780 kPa. In Verbindung mit den Werten der linearen Trockenschwindung von 7,3 % und der Trockenbiegefestigkeit von 9,2 N/mm² ist dieser Ziegelrohstoff ebenfalls als bildsam zu beschreiben. Diese Eigenschaft wird durch den vergleichsweise hohen Tonmineralgehalt und die Kornfeinheit vermittelt. Eine erhöhte Neigung zur Texturbildung ist nicht erkennbar. Die Trockenrissempfindlichkeit und Trocknungsbruchanfälligkeit ist als erhöht zu bewerten.

Durch die Verziegelung der Zusätze wird die Wasserbeladung nur geringfügig beeinflusst. Die Formgebung der Mischungen WBU5 und WBU15 ist mit einer Erhöhung des Presskopfdrucks von 780 auf 890 bzw. 990 kPa verbunden. Die Trockenschwindung wird vermindert. Hinsichtlich der Trockenbiegezugfestigkeit sind keine Festigkeitsverluste festzustellen; tendenziell werden sogar höhere Festigkeiten erzielt. Die Trockenempfindlichkeit ist als mäßig zu einzustufen.

Brennverhalten (Tabellen 5 und 6 und Bild 1)

Ziegelrohstoff VC0

Der Masseverlust von 8,4 % ist auf die Abgabe des Kristallwassers (Tonmineralzersetzung) und auf die Abspaltung des Kohlendioxids der Minerale Calcit und Dolomit zurückzuführen. Der nur geringe Anteil an brennbaren Substanzen hat hierauf keinen Einfluss. Die Brennschwindung ist sehr gering, so dass die Gesamtschwindung (Trocken- und Brennschwindung) nur 6,5 bzw. 6,6 % (linear) beträgt. Dies gilt für Ziegel die in einem Temperaturbereich von 850 bis 920 °C gebrannt werden; eine Erweichung ist nicht festzustellen.

Massebezeichnung		VC0 K 3463		WBU0 K 3465	
Massezusammensetzung		100 M.-%		100 M.-%	
Formgebung		maschinell (mit 90 % Vakuum)			
Reststauchhöhe	mm	24 (28)		24 (27)	
Massesteife (nach Pfefferkorn)	h_0/h_1	1,67		1,67	
Wasserbeladung (Anmachwasser)	M.-%	23,4		24,9	
Presskopfdruck	k Pa	900		780	
lin. Trockenschwindung	%	6,5		7,3	
Trockenbiegezugfestigkeit	N/mm²	7,4		9,2	
Brenntemperatur / Haltezeit	°C/h	850 / 1,0	920 /1,0	850 / 1,0	920 /1,0
Masseverlust	%	8,4	8,4	13,1	13,4
lin. Brennschwindung	%	0	0,1	1,1	1,0
lin. Gesamtschwindung	%	6,5	6,6	8,3	8,2
Erweichung (Umbiegung)	mm	0	0	0	0
Wasseraufnahme	M.-%	17,5	18,0	16,6	17,2
Scherbenrohdichte	kg/dm³	1,83	1,81	1,80	1,78
Tränkungswert	-	0,95	0,96	0,86	0,87
Biegezugfestigkeit	N/mm²	13,5	16,1	20,3	22,1
Druckfestigkeit (40 % LA)	N/mm²	30,6	37,3	40,2	45,6
Scherben-Wärmeleitfähigkeit	W/(m·K)	n.b.	0,522	n.b.	0,431

Tabelle 5: Brenn- und Produkteigenschaften von VC0 und WBU0

Die in Bild 1 dargestellten Dilatometerkurven geben Auskunft über das Dehnungs- und Schwindungsverhalten. Für den Ziegelrohstoff VC0 ist nachfolgend das charakteristische Verhalten aufgeführt.

- Zu Beginn der Aufheizung findet eine thermische Dehnung statt, die im sogenannten Quarzsprungbereich (bei 573 °C) spontan zunimmt.
- Oberhalb von 600 °C wird die thermische Dehnung durch Zersetzungsreaktionen der Tonminerale kompensiert, so dass bis ca. 850 °C nur eine geringe weitere Dehnung erfolgt. Die maximale Dehnung entspricht bei ca. 750 °C einer Längenänderung von 1,1 % (linear).
- Ab etwa 850 °C beginnt der Schwindungsvorgang, der bis 930 °C an Intensität zunimmt. Oberhalb dieser Temperatur ist ein Prozess zu beobachten, der mit einer Widerausdehnung verbunden ist. Dieser Kurvenverlauf wird durch die im Ziegelrohstoff vorhandenen carbonathaltigen Minerale bestimmt, die sich zunächst zersetzen und anschließend als Erdalkalioxide an der Mineralphasenbildung teilnehmen. Die in einem engen Temperaturbereich stattfindende Zwischenschwindung wird auch als Kalksprung bezeichnet.

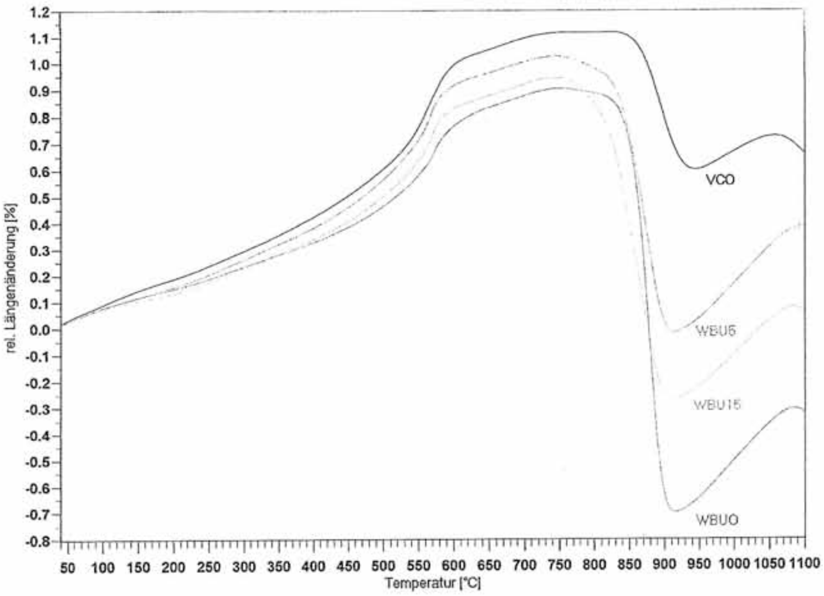

Bild 1: Dilatometerkurven von VC0, WBU0, WBU5 und WBU15

Bei der Beurteilung der an den Prüfziegel ermittelten Brennschwindung (Tabelle 5) ist zu berücksichtigen, dass abweichend von den Bedingungen für die Ermittlung der Dilatometerkurve während des Brandes der Prüfziegel, bei einer Spitzentemperatur von 850 bzw. 920 °C, eine Haltezeit von 1 h eingelegt wird, die die Sinterung des Scherbens beeinflusst. Der Ziegelrohstoff VC0 zeigt keine Neigung zur Reduktionskernbildung.

Massebezeichnung		WBU5 K 3470		WBU15 K 3471	
Massezusammensetzung		100 M.-%		100 M.-%	
Formgebung		maschinell (mit 90 % Vakuum)			
Reststauchhöhe	mm	24 (27)		24 (28)	
Massesteife (nach Pfefferkorn)	h_0/h_1	1,67		1,67	
Wasserbeladung (Anmachwasser)	M.-%	23,6		24,3	
Presskopfdruck	k Pa	890		990	
lin. Trockenschwindung	%	6,9		6,8	
Trockenbiegezugfestigkeit	N/mm^2	10,1		9,4	
Brenntemperatur / Haltezeit	°C/h	850 / 1,0	920 /1,0	850 / 1,0	920 /1,0
Masseverlust	%	12,7	13,0	12,7	12,9
lin. Brennschwindung	%	0,9	0,8	1,0	0,9
lin. Gesamtschwindung	%	7,7	76,6	7,7	7,6
Erweichung (Umbiegung)	mm	1,0	1,0	0,5	0,5
Wasseraufnahme	M.-%	18,3	18,6	19,3	19,6
Scherbenrohdichte	kg/dm^3	1,79	1,78	1,76	1,76
Tränkungswert	-	0,89	0,90	0,91	0,92
Biegezugfestigkeit	N/mm^2	14,4	15,1	12,5	14,3
Druckfestigkeit (40 % LA)	N/mm^2	33,5	35,1	33,8	36,7
Scherben-Wärmeleitfähigkeit	W/(m·K)	n.b.	0,450	n.b.	0,424

Tabelle 6: Brenn- und Produkteigenschaften von WBU5 und WBU15

Ziegelrohstoff WBU0 und Mischungen WBU5 und WBU15

Anhand der ebenfalls in Bild 1 dargestellten Dilatometerkurven wird ersichtlich, dass WBU0 eine geringere maximale Dehnung von 0,9 % (linear) aufweist, jedoch der anschließende Prozess durch eine in seiner Intensität und Größe ausgeprägte Zwischenschwindung und verstärkte Widerausdehnung zu charakterisieren ist. Ursächlich hierfür sind einerseits der geringe Gehalt an freiem Quarz und der höhere Gehalt carbonathaltiger Minerale. Durch den Zusatz wird der Ausdehnungsprozess verstärkt und das Maß der Zwischenschwindung reduziert. Neben einem vergleichsweise höheren Masseverlust sind je nach der Höhe der Brenntemperatur lineare Brennschwindungen von 1,1 bzw. 1,0 % an den Prüfziegeln festzustellen. Diese werden durch die Zusätze nur geringfügig verringert. Hierbei ist im Vergleich zur Dilatometerkurve ebenfalls der Einfluss der Haltezeit auf die Sinterung zu berücksichtigen. Eine Erweichung ist nur im geringen Umfang aufgetreten. Eine Neigung zur Reduktionskernbildung ist nicht festzustellen.

Produkteigenschaften (Tabellen 5 und 6; Bilder 2 und 3)

Ziegelrohstoff VC0

Nach Brand bei einer Spitzentemperatur von 850 °C, hat der Scherben eine Wasseraufnahme von 17,5 Massen-% und eine Scherbenrohdichte von 1,83 kg/dm³. Eine Erhöhung der Brenntemperatur ist mit einer geringfügigen Leichterung verbunden, die sich in einer höheren Wasseraufnahme von 18,0 Massen-% und einer niedrigeren Scherbenrohdichte von 1,81 kg/dm³ äußert. Der hohe Tränkungswert von 0,96 bzw. 0,95 lässt erkennen, dass ein Großteil des Porenvolumens schon bei der Wasserlagerung unter Atmosphärendruck gefüllt wird. Demnach steht für die Eisbildung nur ein geringer Ausweichporenraum zu Verfügung. Der Scherben ist als frostgefährdet einzustufen.

Die mit 850 °C gebrannten Scherben haben eine Biegezugfestigkeit von 13,5 N/mm² und eine Druckfestigkeit von 30,6 N/mm². Die Festigkeit unter Biegezug- als auch Druckbeanspruchung wird durch den Brand bei höheren Temperaturen verstärkt. Eine Beurteilung der Festigkeitswerte wird noch in einer zusammenfassenden Darstellung vorgenommen. Dies gilt auch für die Scherben-Wärmeleitfähigkeit, die mit einem Wert von 0,522 W/(m·K) zu kennzeichnen ist. Ausblühungen sind an den gebrannten Scherben, nach Wasserlagerung und anschließender Trocknung nicht aufgetreten.

Ziegelrohstoff WBU0 und Mischungen WBU5 und WBU15

Nach Brand bei einer Spitzentemperatur von 850 °C, hat der Scherben eine Wasseraufnahme von 16,6 Massen-% und eine Scherbenrohdichte von 1,80 kg/dm³. Eine Erhöhung der Brenntemperatur ist ebenfalls mit einer geringfügigen Leichterung verbunden. Trotz vergleichsweise niedrigerer Tränkungswerte von 0,86 bzw. 0,87 ist der Scherben noch als frostgefährdet einzustufen.

Die mit 850 °C gebrannten Scherben haben eine Biegezugfestigkeit von 20,3 N/mm² und eine Druckfestigkeit von 40,2 N/mm². Die Festigkeit unter Biegezug- als auch Druckbeanspruchung wird durch Anwendung höherer Brenntemperaturen verstärkt. Die Scherben-Wärmeleitfähigkeit ist mit einem Wert von 0,431 W/(m·K) zu kennzeichnen. Ausblühungen treten nicht auf.

Durch den Zusatz wird die Wasseraufnahme nur geringfügig erhöht und die Scherbenrohdichte unwesentlich niedriger. Das Scherbengefüge gestaltet sich im Vergleich zum unbezuschlagten Ziegelrohstoff WBU0 offenporiger, so dass die Bedingungen für die Frostwiderstandsfähigkeit negativ beeinflusst werden. Die Leichterung des Scherbens ist mit einer Festigkeitsabnahme verbunden. Eine Herabsetzung der Scherben-Wärmeleitfähigkeit ist nur im Falle der Mischung WBU15 gegeben.

Den Ergebnissen der chemischen Untersuchungen (Prüfbericht Nr. CH 6811) zufolge, wird der Sulfat- und Pyritschwefelgehalt in den Mischungen WBU5 und WBU15 erhöht. Der Ausblühtest an den gebrannten Ziegeln zeigt weißliche Ablagerungen nach Wasserlagerung, die auf wasserlösliche Salze im Scherben zurückzuführen sind. Zudem sind schon am getrockneten, also ungebrannten Rohling Trockenausblühungen (Calci-

umsulfatausblühungen) zu erkennen, die nach Brand mit einer irreversiblen hellen Färbung des Scherbens verbunden sind.
Zur Beurteilung der nach Brand bei einer Temperatur von 920 °C erzielten Produkteigenschaften ist in einer Gesamtdarstellung der Ergebnisse im Bild 2 neben den hier ermittelten Druckfestigkeiten der Ziegelrohstoffe und Mischungen eine Vielzahl von Festigkeitswerten unterschiedlicher Betriebsmassen ergänzend angegeben. Eine Herabsetzung der Scherbenrohdichte ist prinzipiell mit einem Festigkeitsverlust verbunden, jedoch sind bei gleicher Scherbenrohdichte auch beachtliche Unterschiede im Festigkeitsniveau zu erwarten.

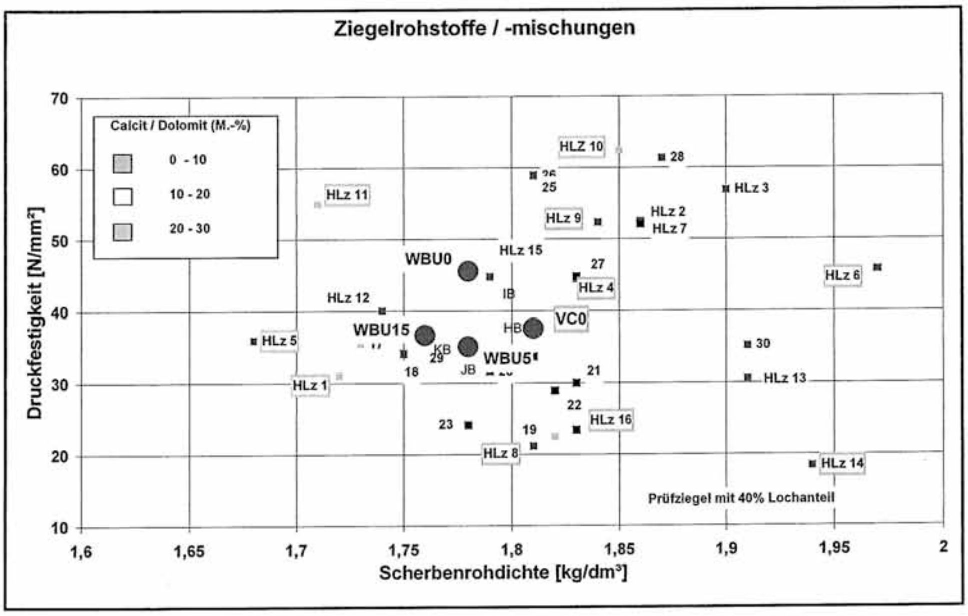

Bild 2: Druckfestigkeit von VC0, WBU0, WBU5 und WBU15

Die Ergebnisse der unbezuschlagten Ziegelrohstoffe VC0 und WBU0 sind bei einer Scherbenrohdichte von 1,81 bzw. 1,78 kg/dm^3 einem mittleren Festigkeitsniveau zuzuordnen, wobei die erzielten Festigkeiten unter Berücksichtigung eines Lochanteils von 40 % im Mittel 37,3 bzw. 45,0 N/mm^2 betragen. Die Mischung WBU5 mit 5 % Zusatz hat bei einer Scherbenrohdichte von 1,78 kg/dm^3 eine Festigkeit von 35,1 N/mm^2. Bei einer Zugabe von 15 % in Mischung WBU15, wird bei einer niedrigeren Scherbenrohdichte von 1,76 kg/dm³ eine Festigkeit von 36,7 N/mm² erreicht. Der Festigkeitsabfall entspricht der Tendenz, die durch die Abhängigkeit der Festigkeit von der Scherbenrohdichte dargestellt wird.

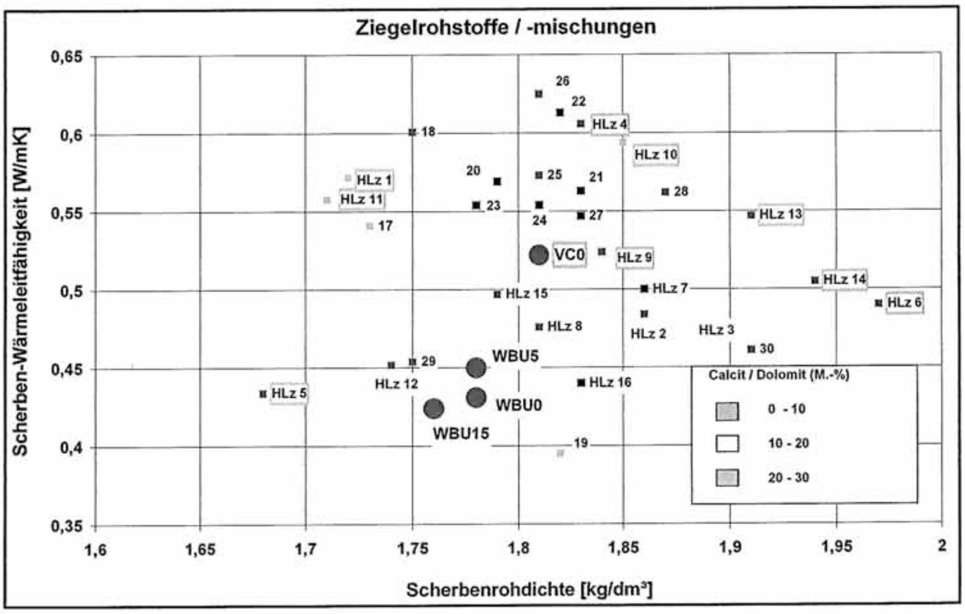

Bild 3: Scherbenwärmeleitfähigkeit von VC0, WBU0, WBU5 und WBU15

In Bild 3 sind ebenfalls für eine Vielzahl von Betriebsmassen die Scherben-Wärmeleitfähigkeiten in Abhängigkeit von der Scherbenrohdichte dargestellt, in der die Werte für die hier untersuchten Ziegelrohstoffe und Mischungen enthalten sind. Dieser Darstellung entsprechend ist der Ziegelrohstoff VC0 mit einer Wärmeleitfähigkeit von 0,522 W/(m·K) einem mittleren Bereich zuzuordnen. Der Ziegelrohstoff WBU0 liegt mit 0,431 W/(m·K) in einem günstigen Bereich, der gute Wärmedämmwerte erwarten lässt. Im Falle der Mischung WBU15 wird die Voraussetzung für eine verbesserte Wärmedämmung noch begünstigt.

Essen, 12. Juni 2009
ru/do

Der Institutsleiter:

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Untersuchungen zur Geruchsminderung beim Einsatz von Papierfangstoff

Forschungsbericht 072/00

von Dipl.-Ing E. Rimpel

Essen, Juli 2003

1. Einleitung

Papierfangstoff – ein Restprodukt der Papierindustrie – ist derzeit eines der am häufigsten eingesetzten Porosierungsmittel bei der Herstellung von Mauerziegeln. Aus technischer Sicht bietet Papierfangstoff einige günstige Eigenschaften, wie z.B. Minderung der Trockenbruchempfindlichkeit. Auf der anderen Seite beginnt Papierfangstoff bei Lagerung sehr leicht zu gären. Neben Veränderungen der Fangstoffeigenschaften können erhebliche Geruchsemissionen auftreten. Während einerseits durchaus wünschenswerte Effekte durch die Lagerung von aufbereiteten Ziegelmassen denkbar sind und deren gezielte Nutzung angestrebt wird, ist derzeit in den meisten Fällen davon auszugehen, dass der Ziegler die Unterdrückung der biologischen Abbauvorgänge und der Geruchsemissionen anstrebt. Hierzu wird dem Papierfangstoff beispielsweise Kalkmilch (Suspension von Kalziumhydroxid in Wasser) zugegeben. Unklar ist derzeit die benötigte Menge, die Wirkungsdauer und die Frage, ob Papierfangstoffe unterschiedlicher Herkunft ein unterschiedliches Gärungspotential aufweisen. Darüber hinaus erscheint es wünschenswert, durch möglichst einfache Mittel die Gärungsgefährdung zu verhindern oder zu vermindern und so die Geruchsemissionen zu vermeiden.

Ziel des Vorhabens ist es, die Bedingungen zu untersuchen, mit denen eine geruchsintensive Gärung von Papierfangstoff zuverlässig und praxisnah verhindert werden kann.

2. Problemstellung

Wie bei allen Zusatzstoffen, insbesondere bei Reststoffen aus anderen Industriezweigen, muss man beim Einsatz zwischen den rechtlich zulässigen, den technisch machbaren und den durch den Markt und bei der Herstellung akzeptablen Möglichkeiten unterscheiden.

Bei den Reststoffen, die die Papierfabriken verlassen, handelt es sich in der Regel um Abfälle im Sinne des Kreislaufwirtschafts-/ Abfallgesetzes (KrW-/AbfG), da sich nach §3 I S.1 der „Besitzer“ dieser Stoffe entledigt, entledigen will oder entledigen muss. Gleichzeitig schreibt dieses Gesetz in §2 auch vor, dass Abfälle in erster Linie zu vermeiden und in zweiter Linie zu verwerten sind. Dieses kann zum einen durch die stoffliche Verwertung gem. §4 III Krw-/AbfG durch die Substitution von primären Rohstoffen, durch das Gewinnen von Stoffen aus Abfällen oder die Nutzung der stofflichen Eigenschaften von Abfällen geschehen und zum anderen gemäß §4 IV Krw-/AbfG durch die energetische Verwertung. Hierbei muss der Abfall Stoffeigenschaften eines Ersatzbrennstoffes aufweisen und als solcher, d.h. zur Energienutzung, eingesetzt werden. Da Papierfangstoff einen Energieinhalt zwischen 6 – 13 MJ/kg besitzt und sich somit zur Mitverbrennung eignet, ist es wichtig festzustellen, dass es sich beim Einsatz in Ziegelwerken nicht um eine Mitverbrennung zur Energiesubstitution handelt (diese würde nach 17. BlmSchV mit entsprechenden Anforderungen behandelt), sondern um eine stoffliche Verwertung zur Porosierung von Ziegeln. Das bedeutet, dass nicht die Wärmeentwicklung bei der Ausgasung der organischen Komponenten, sondern die Bildung von Hohlräumen zur Porosierung der Grund des Einsatzes ist. In diesem Fall gelten lediglich, wie im üblichen Ziegeleibetrieb, die Anforderungen der TA-Luft.

Aus technischer Sicht bietet Papierfangstoff einige günstige Eigenschaften, wie z.B. die erwähnte Minderung der Trockenbruchempfindlichkeit, da der Papierfangstoff die Rohlingsmasse durch seine faserige Struktur während der Trocknung armiert. Er ist somit als Produktionshilfe zu sehen. Weiterhin kann er die Produkteigenschaften positiv beeinflussen, da er durch Bildung von Hohlräumen bei der Aufheizung der Ziegel für eine feine Porosierung und somit zur Verbesserung der Wärmedämmeigenschaften der Ziegel führt. Im Gegensatz zu „reinen“ Porosierungsstoffen, wie z.B. Polystyrol oder Sägemehl, kann Papierfangstoff durch die bei der Papierherstellung zur Glättung der Papieroberfläche verwendete Kreide eine gewisse Menge an Kalziumkarbonat liefern, das zu einer Verbesserung der Druckfestigkeit von hochporosierten Ziegeln beitragen kann. Des weiteren kann durch den Heizwert des Fangstoffes in begrenztem Maße fossile Energie eingespart werden. Um alle diesen positiven Eigenschaften nutzen zu können, muss der Fangstoff in konstanter Qualität vorliegen.

Die Qualitätsforderung an die Fangstoffe bezieht sich zum einen auf die Struktur der Fasern und den Anteil an Streichmitteln, um die für die Ziegelqualität notwendigen Parameter beizubehalten, zum anderen aber auch auf die Schadstoffbeladung, hier seien in erster Linie Schwermetall- und Chlorgehalte angesprochen. Die Schwermetalle werden zwar zum überwiegenden Teil keramisch eingebunden, führen aber beim Genehmigungsverfahren zu Diskussionen; zu hohe Chlorgehalte im Fangstoff führen nicht nur zu Chlorwasserstoffemissionen, sondern im Falle von Taupunktunterschreitungen im

Nach einem Tag wurde versucht, das subjektive Empfinden mit objektiven Messungen zu belegen, indem die Emission von Gesamtkohlenstoff, als ein Indiz für ablaufende Gärungsprozesse, über dem Fangstoff gemessen wurde. Die Messungen zeigen (bis auf eine Ausnahme bei Probe P 1937) das gleiche Ergebnis wie die Geruchsprüfung.

Probe	Geruch	Messwert [mg C_{ges}/m^3]	pH-Wert
P 1933	neutral	0,11	9,0
P 1934	leicht	8,25	10,1
P 1935	leicht	7,46	11,0
P 1936	intensiv	13,26	7,6
P 1937	intensiv	1,23	8,1
P 1938	stark	32,0	7,4

Tabelle 2: Vergleich der subjektiven Geruchsprobe mit Messwerten

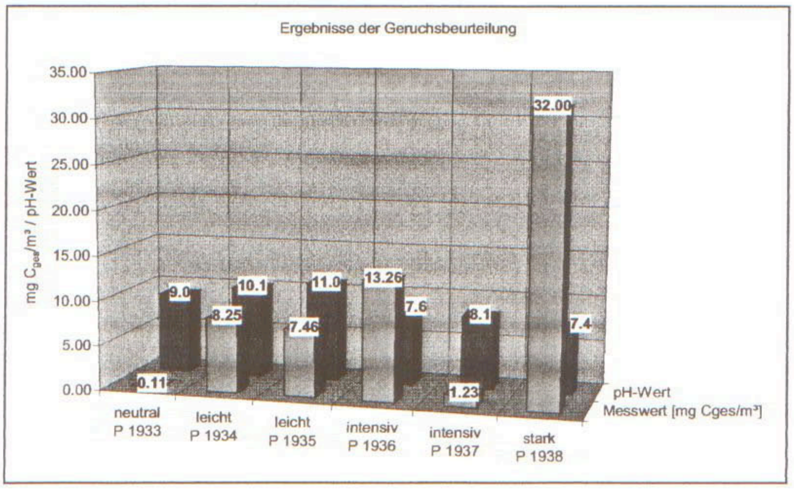

Bild 1: Vergleich der subjektiven Geruchsprobe mit Messwerten

Um die Geruchsemissionen zu vermindern oder zu verhindern, wurden die verschiednen Fangstoffe zum einen mit Kalkmilch behandelt und zum anderen mit einer quartären Ammoniumverbindung.

Bei Kalkmilch handelt es sich um eine dünne Aufschlämmung von Kalziumhydroxid mit Wasser. Sie führt bei der Zugabe zum Fangstoff zur Erhöhung des pH-Werts, d.h. zur Schaffung eines alkalischen, bakterienfeindlichen Milieus, so dass die Zersetzung der organischen Bestandteile des Fangstoffs nicht stattfinden kann.

Quartäre oder quaternäre Ammoniumverbindungen ist die Bezeichnung für organische Ammoniumverbindungen. Es sind Salze oder Basen, in deren Ammoniumgruppe (NH_4) alle vier H-Atome durch organische Reste (CH_{3}-, C_2H_5- u. dgl.) ersetzt sind. Sie haben stark desinfizierende Wirkung und zeigen grenzflächenaktive Eigenschaften, so dass sie z.B. auch in Reinigungsmitteln, Haarspülmitteln oder Waschmitteln Verwendung finden. Handelsübliche, für die Bekämpfung von Geruchsemissionen eingesetzte quartäre Ammoniumverbindungen sind Enzypur G und Bioton. Enzypur G wird in der Papier- und Zuckerindustrie, in Kläranlagen und zur Schlammbehandlung eingesetzt. Bioton ist ein Additiv zur Behandlung von ARA-Schlämmen der Papierindustrie und wird ebenfalls erfolgreich zur Vermeidung von Geruchsemissionen aus Klärschlämmen verwendet. Für die hier durchgeführten Versuche wurde eine Mischung aus Bioton A1/3 und Bioton S verwendet. Durch das Vorhandensein von Terpen, einem charakteristisch riechenden leichten ätherischen Öl, entsteht der im folgenden als fruchtig bezeichnete Geruch.

Nach der Behandlung der verschieden Fangstoffe wurden diese in feuchter Atmosphäre bei Raumtemperatur gelagert, und in zeitlichen Abständen wurden subjektiv die Geruchsemission und mögliche Belästigung durch Riechen bestimmt.

Die Ergebnisse der mit Kalkmilch behandelten Fangstoffe sind in Tabelle 3 zusammengefasst. Die Intensität des Geruchs ist durch Kreuze gekennzeichnet, je intensiver der Geruch umso mehr Kreuze wurden vergeben. „+-„ bedeutet, dass keine Geruchsemission festzustellen war, „muffig“ beschreibt einen unangenehmen, jedoch papieruntypischen Geruch nach Fäulnis und NH_4 einen Geruch nach Ammoniak.

Zusatzmittel: Kalkmilch

Lagerdauer [Tage]	P1933	P1934	P1935	P1936	P1937	P1938
0	x	xx	xx	xxx	xxx	xxxx
5	x	x	x	xxx	xxx	xxxx
12	+-	+-	+-	xxx	xxx	xxxx
19	+-	+-	+-	+-	+-	xxxx
26	+-	+-	+-	muffig	muffig	xxxx
33	+-	+-	+-	muffig	muffig	NH_4
41	+-	+-	+-	muffig	muffig	NH_4
48	+-	+-	+-	muffig	muffig	NH_4
54	+-	+-	+-	muffig	muffig	NH_4

Tabelle 3: Ergebnisse der Geruchsemission bei der Lagerung von Fangstoffen nach Zugabe von Kalkmilch

Es ist zu erkennen, dass die „frischen" Fangstoffe mit der Kalkmilch geruchsneutral gelagert werden konnten. Es bildete sich lediglich nach etwa 14 Tagen ein mehr oder weniger ausgeprägter Schimmelbelag, der aber nicht zu Gerüchen führte.

Ganz anders stellt sich die Situation bei den durch einen Entsorger angelieferten Fangstoffen dar. Hier veränderte sich die Intensität des Geruchs zunächst überhaupt nicht. Die kurze Dauer der Geruchsneutralität bei den Proben P 1936 und P 1937 ist wohl darauf zurückzuführen, dass die Organik durch die bakterielle Zersetzung komplett aufgezehrt war bevor die Proben anfingen papieruntypisch muffig zu riechen. Die Probe P 1938 war durch Kalkmilch geruchsmäßig überhaupt nicht zu neutralisieren und begann nach etwa 30 Tagen nach Ammoniak zu riechen.

In einer weiteren Versuchsreihe wurden die Fangstoffe mit einer Mischung aus quaternären Ammoniumverbindungen besprüht, die unter den Handelsnamen Bioton S und Bioton A1/3 zu erhalten sind. Der fruchtige Geruch der Massen wird durch die Verwendung von Terpenen (ätherischen Ölen) im Bioton hervorgerufen. Die Ergebnisse sind in Tabelle 4 zusammengefasst.

Lagerdauer [Tage]	quaternäre Ammoniumverbindungen P1933	P1934	P1935	P1936	P1937	P1938
0	fruchtig	fruchtig	fruchtig	fruchtig	fruchtig	fruchtig
4	fruchtig	fruchtig	fruchtig	fruchtig	fruchtig	fruchtig
6	fruchtig	fruchtig	fruchtig	fruchtig	fruchtig	fruchtig
11	fruchtig	fruchtig	fruchtig	fruchtig	fruchtig	fruchtig
18	fruchtig	fruchtig	fruchtig	fruchtig	fruchtig	fruchtig
25	fruchtig	fruchtig	fruchtig	fruchtig	fruchtig	fruchtig
31	+-	+-	+-	muffig	+-	+-
38	+-	+-	+-	muffig	+-	NH_4
44	+-	+-	+-	muffig	muffig	NH_4
51	+-	+-	+-	muffig	muffig	NH_4
57	+-	+-	+-	muffig	muffig	NH_4

Tabelle 4: Ergebnisse der Geruchsemission bei der Lagerung von Fangstoffen nach Zugabe von quartären Ammoniumverbindungen (Bioton)

Wie zu erkennen ist, kann durch die Behandlung der Fangstoffe mit quartären Ammoniumverbindungen die Geruchsbelästigung über lange Zeit vermieden werden. Selbst bei den zuvor intensiv oder übelriechenden Fangstoffen des Entsorgers wurde der Geruch über mehr als 30 Tage unterdrückt. Es ist anzumerken, dass der Gestank der Fangstoffe durch den fruchtigen Geruch der Ammoniumverbindungen nicht überdeckt, sondern beseitigt wird.

Die „frischen“ Fangstoffe fingen auch nach längerer Lagerzeit und nachlassender Wirkung der Ammoniumverbindungen nicht an zu riechen, lediglich die vom Entsorger angelieferten Fangstoffe entwickelten, wie bei der Kalkmilchzugabe, die muffigen bzw. nach Ammoniak riechenden Emissionen, jedoch nach deutlich längerer Lagerzeit als bei der Kalkmilch.

Die Behandlung der Fangstoffe mit quartären Ammoniumverbindungen stellt eine gangbare Möglichkeit dar, Geruchsemissionen durch Fangstoffe zu vermeiden. Der Einsatz von Bioton wird in einem dem Institut bekannten Ziegelwerk mit großem Erfolg eingesetzt. Hier wird nicht nur Fangstoff sondern auch kommunaler Klärschlamm mit Bioton behandelt und verziegelt, ohne dass es bei der Lagerung, der Aufbereitung oder im Trockner zu irgendwelchen Geruchsemissionen kommt. Wichtig ist dabei, und das zeigen auch die Versuche an den unterschiedlichen Fangstoffen (fabrikfrisch oder vom Entsorger), dass die Behandlung schon in der Papierfabrik geschieht. Werden die quartären Ammoniumverbindungen erst im Ziegelwerk zugegeben, so muss (nach Erfahrungen im Ziegelwerk) die Zugabemenge etwa 20-mal so hoch sein. Nach Aussagen des Betreibers des Ziegelwerkes betragen die Kosten für den Einsatz von Bioton direkt in der Papierfabrik etwa 1,50 €/t Fangstoff.

4. Zusammenfassung

Immer wieder kommt es beim Einsatz von Papierfangstoffen bei der Ziegelherstellung zu Problemen mit Geruchsemissionen. Im Rahmen des Forschungsvorhabens wurden Möglichkeiten zur Geruchsvermeidung untersucht, und mit dem Einsatz von quartären Ammoniumverbindungen konnte ein gangbarer Weg aufgezeigt werden, diese Gerüche zu verhindern. Ziegelwerke, die Geruchsemissionsprobleme durch Fangstoffe haben, sollten sich bei Direktanlieferung an das Papierwerk wenden, oder im anderen Fall über den Entsorger an das Papierwerk, damit die Behandlung direkt im Papierwerk stattfinden kann. Immerhin werden 24 % der anfallenden Fangstoffe in die Ziegelindustrie verbracht, eine Deponierung von unbehandeltem Fangstoff ist nach der neuen TA-Siedlungsabfall nicht mehr gestattet, und im Bereich der Kompostierung treten Akzeptanzprobleme auf, so dass eine solche Kooperation zwischen Ziegelwerk und Papierfabrik möglich sein sollte.

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