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Modelling and conceptual design of a waste smelting process

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Abstract

A pyrometallurgical process has been modelled and conceptually designed for the thermal treatment of heavy metal containing waste streams like MSW incinerator fly ash and sewage sludge. The modelling is carried out using the computer program EQUIMET as developed by Billiton Research BV. This program calculates thermodynamic equilibrium, making use of a slag model to account for the non-ideality of the slag phase. By comparison with a pilot test on smelting of MSW incinerator fly ash it is shown that thermodynamic modelling reasonably describes the waste smelting process and especially the fate of the minor elements. The thermodynamic model has been incorporated into a flow sheeting program, which calculates energy and mass balances for the proposed process configuration. Calculations show that it is possible to produce a clean slag phase, meeting recycling requirements. The heavy metal containing residues can be processed for further recycling.

Keywords: Pyrometallurgical process; Heavy metal; Thermal treatment; Thermodynamic equilibrium; Fly ash; Sewage sludge

1. Introduction

The disposal of solid wastes contaminated with heavy metals via landfill is causing more and more environmental problems and, combined with the shortage of landfill sites, calls for a more environmentally sound method of disposal. A sustainable solution can be reached by putting great effort into waste prevention. However, since total prevention of waste is impossible, a sustainable method for waste processing has to be developed. The best method to deal with this problem is to convert the wastes into useful products. In order to make

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these products from heavy metal contaminated waste streams, the metals have to be removed or immobilized. This can be done either pyrometallurgically, i.e., via high temperature processing, or hydrometallurgically, i.e., processing in the aqueous phase. Whereas the latter processes are rather sensitive to changes in feed composition and require a process development effort for each waste stream separately, the former can be applied to a wide range of wastes.

Apart from the widespread usage of metalliferous (largely in industry generated) waste streams in the metallurgical industry, the only high temperature process specifically in operation for the smelting of solid (non-metallic) wastes is the Kubota process which operates in Japan [1,2]. Many investigations have been performed to develop waste smelting processes, both for MSW (municipal solid waste) incinerator fly ash and sewage sludge [3–7]. Most of these focused on vitrification. The vitrified slag, however, has only limited use and the risk that (eventually) pollutants are released remains.

In contrast to vitrification, a more sustainable solution is to prepare a clean slag phase, which contains no pollutants any more and can readily be used. As in general inert compounds like SiO_2 , Al_2O_3 and CaO make up for over 90% of heavy metal containing waste streams the slag is by far the largest product from a waste smelting process. A promising pyro-metallurgical technique is the so-called oxy-smelt process [8,9], in which such a clean slag is produced. Uses for these slags are to be found in, e.g., construction, raw material for cement, etc. The heavy metals are concentrated in a flue dust and a metal (mainly iron) phase which potentially can be used by the metallurgical industry. The flue dust can, e.g., be used (after water wash) as input for an electrolytic smelter, thus recovering Zn and Cd or be used as feed for a Waelz kiln.

This study deals with the modelling and conceptual design of a smelting process for the treatment of wastes contaminated with heavy metals. As examples MSW incinerator fly ash and sewage sludge have been selected.

2. Waste smelting process

Fig. 1 depicts a schematic flow sheet of the proposed smelting process. In principle the process can be divided into three parts: feed section; reactor section; and flue gas cleaning section.

In the feed section the waste is pretreated as far as necessary to enable feeding to and smelting in the reactor section. Additives are mixed with the feed to control the slag phase composition, which in turn determines the smelting characteristics of the waste stream. The amount of additives required depends on the desired viscosity, liquidus temperature and crystallisation behaviour of the slag. Fig. 2 shows the compositions of the used waste streams, normalised to the ternary system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$, and their viscosities at 1723°K. Viscosity is one of the most important factors to ensure smooth operation of the smelting furnace. In particular, the ease of handling of the slag phase largely depends on the slag viscosity at the tapping temperature. By adding CaO (in the form of CaCO_3) it is (in these cases) possible to lower the viscosity to below 10 N s m^{-2} , a value at which the slag can be routinely handled. For example, incinerator fly ash of this particular composition requires the addition of 180 kg CaCO_3 per ton in order to reach acceptable melting and viscosity

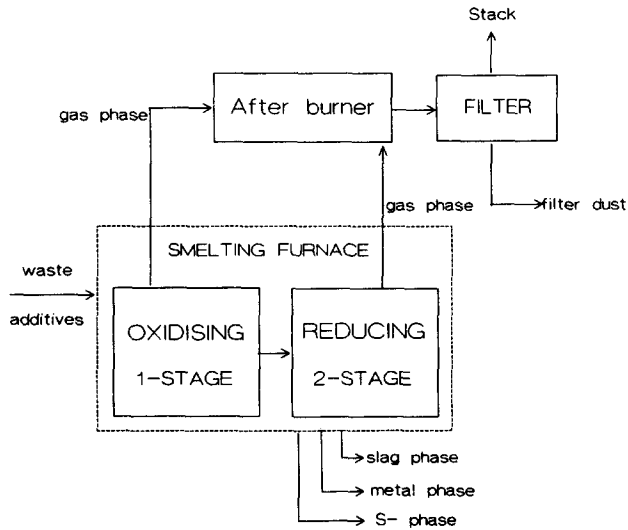


Fig. 1. Process scheme waste smelting process.

behaviour. In Fig. 2 the resulting mixture compositions and their viscosities are also indicated.

Addition of additives like CaO obviously also controls the composition of the product slag. This is an important parameter for the desired ultimate use of the slag as, e.g., cement raw material or the production of mineral fibres.

The reactor section consists of a smelting furnace, which is more or less separated into two zones: first an oxidising stage in which most of the heating is carried out, followed by a reducing stage in which the metals are removed from the slag. An example of such a furnace would be the KHD cyclone furnace, which in the metallurgical industry is used for

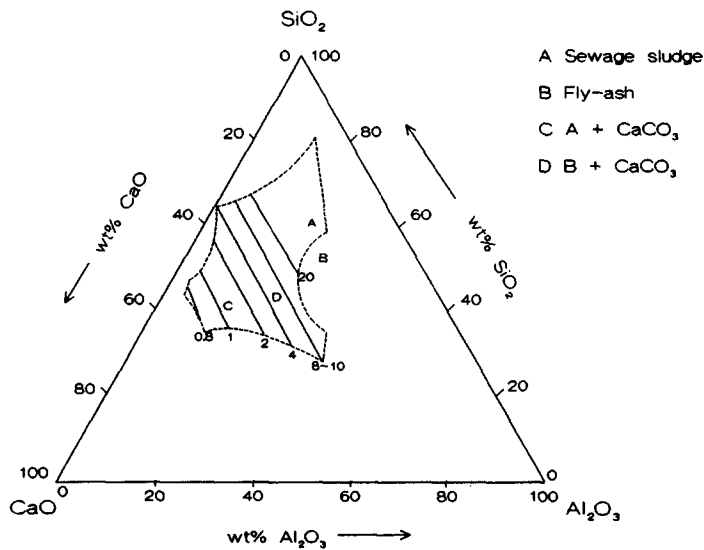


Fig. 2. Viscosity ($N s m^{-2}$) for fly-ash and sewage sludge at 1723°K.

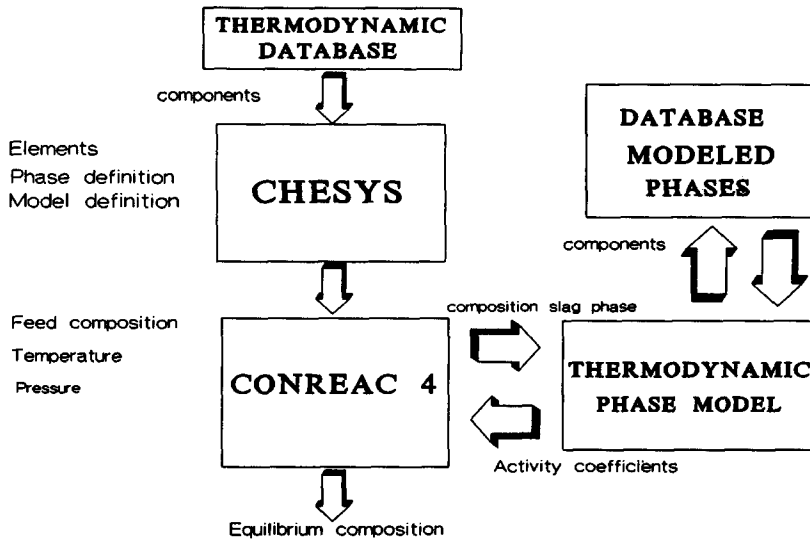


Fig. 3. Flow chart of the Equimet computer program.

smelting of flue dusts from, e.g., copper smelting. Reduction is accomplished by adding coal. Normal waste smelting temperatures would vary from 1623 to 1873°K. At these temperatures and by controlling other process parameters like oxygen pressure and feed composition, it is possible to generate a clean slag phase via this two-stage oxidative-reductive smelting route.

In the oxidising stage most of the volatile heavy metals (and salts like NaCl) are evaporated and the organic compounds burned. The flue dust from this stage can be used as raw material to recover the zinc and lead, etc. [10].

In the reducing stage the last traces of the volatile metals are removed. Furthermore, a metal phase is formed. The latter contains iron and other non-volatile metals like Ni, Co, Cr and Mn. This iron phase can conceivably be used in the metallurgical industry, e.g., as raw material in stainless steel recycling operations.

The gas treatment section consists of a waste heat boiler by which most of the heat is recovered and a filter system in which the volatile metals, notably Zn, Pb and Cd are collected in the form of an oxidised flue dust. By operating the furnace with oxygen in stead of air low NO_x emissions are possible.

3. Process modelling

The waste smelting process can, due to the high temperatures involved causing kinetic barriers to be largely absent, be adequately described by means of a thermodynamic model. This was performed by the EQUIMET computer program from Billiton Research BV, which is schematically shown in Fig. 3.

The program calculates overall thermodynamic equilibrium with up to 15 elements divided over 98 components. It consists of two subprograms called CHESYS and CONREAC4. Within CHESYS the chemical system is defined and required data collected from

a thermodynamic database. CONREAC4 subsequently carries out the thermodynamic calculation. It makes use of the SOLGASMIX routine developed by Eriksson [11], calculating the equilibrium composition by minimizing the Gibbs free energy of the total system. This technique is especially suited for calculation of the distribution of trace elements over the various phases (gas, slag, metal) involved [12].

A very important feature of the EQUIMET program is the possibility to introduce (thermodynamic) non-ideality into the system, as especially slags are highly non-ideal. Therefore the choice of a correct slag model is crucial. EQUIMET contains a highly sophisticated slagmodel [13]. This model is based on the concept of a silica network, which can be modified or broken by interaction with other elements. The network breakers (e.g., Ca, Na, Mg) will break up the three-dimensional silica network and therewith influence both the thermodynamic activities of the components of the slag and its physical properties like viscosity. Next to these, there are also elements which can act as network breaker as well as former (e.g., Al). The model consists of a statistical thermodynamic description, together with energy functions for the interactions which have been derived from experimental (primarily binary phase diagram) data [14].

The slag model calculates the activity coefficients for the slag components at a certain composition. With these activity coefficients a new equilibrium is calculated by means of CONREAC4. This new equilibrium composition is fed back to the slag model which in turn generates a new set of activity coefficients. This procedure is repeated until there is no significant change in composition any more, thus iteratively arriving at a slag composition consistent with calculated thermodynamic activity coefficients.

In addition to the above thermodynamic calculations, the actual process modelling was performed by the computer program BICEPS from Billiton Research BV. This is a relatively simple flowsheeting program, in which CONREAC4 is integrated as reactor model. Unfortunately, the slag model can not be directly incorporated into this program. However, for the actual examples chosen, this is no problem for the calculations, as previous studies [15] have shown that, due to the low concentrations of impurities in these waste streams, it is possible to regard the activity coefficients as constants. The procedure then consists of calculating, by means of the slag model, the activity coefficients of the components in the bulk composition of the slag and using these as constants within BICEPS to generate mass and energy balances.

4. Results

Modelling has been performed for two waste streams: incinerator fly ash and sewage sludge. Table 1 shows the input composition of these waste streams and the amount of CaCO_3 added which is needed in order to reach an acceptable smelt. The most important differences between these waste streams are the amounts of organic material (61 wt% for sewage sludge), the water content and the amount of Cl, S and P.

The results of the reactor model (CONREAC4) for the smelting of MSW incinerator fly ash are depicted in Fig. 4. By plotting the concentration of trace elements in the slag phase as function of the oxygen partial pressure, it can be shown at which oxygen partial pressure

Table 1
Composition of incinerator fly-ash and sewage sludge waste streams

Component	Fly-ash		Sewage sludge	
	g/kg	mol/kg	g/kg dry solids	mol/kg dry solids
SiO ₂	304.0	5.061	169.0	2.813
CaO	111.0	1.979	46.2	0.824
Al ₂ O ₃	206.0	2.021	61.5	0.603
MgO	2.78	0.069	7.0	0.173
Na ₂ O	68.98	1.113	5.2	0.084
K ₂ O	–	–	6.0	0.064
P ₂ O ₅	–	–	52.5	0.370
BaO	2.91	0.019	–	–
TiO ₂	–	–	–	–
FeO	3.30	0.046	–	–
Fe ₂ O ₃	–	–	39.6	0.248
MnO	1.70	0.024	–	–
CdO	0.30	0.0017	0.0057	0.0004
As ₂ O ₃	0.26	0.0013	0.0198	0.0001
PbO	6.14	0.0275	0.2961	0.0013
ZnO	17.4	0.2141	1.9211	0.0236
SnO	0.62	0.0457	0.1341	0.0010
Cu ₂ O	1.21	0.0084	0.6101	0.0043
NiO	0.13	0.0017	0.0368	0.0005
Cr ₂ O ₃	0.34	0.0023	0.1071	0.0007
S	36.38	1.134	5.19	0.305
Cl	70.97	2.002	5.09	0.159
C	32.0	2.664	298.0	24.831
H	–	–	47.2	47.2
O	78.52	4.908	216.3	13.52
N	–	–	35.8	2.56
F	3.60	0.1895	–	–
H ₂ O	34.55	1.919	111.1	6.172
Total	1000.4		1111	
CaCO ₃ ^a	179.0	1.788	275.0	2.747

^aAdded (g CaCO₃/kg dry solids).

trace elements can be removed, that is how reducing the furnace has to be operated in order to arrive at a certain slag quality in terms of 'cleanliness'.

At decreasing oxygen pressure, first the volatile elements Zn, Cd and Pb are removed to the gas phase as metal vapours (Zn, Cd, Pb) or compounds (PbO). In order to avoid problems with pyrophoric dusts arising from the condensation of these metal vapours in the gas treatment unit, at some point the oxygen pressure has to be increased to oxidize the metal vapours back to their oxides. After this oxidation the flue dust is collected and can be regarded as raw material for recycling of, in particular, zinc and lead.

Lowering the oxygen pressure further, a metallic (Fe) phase is produced, which accumulates at the bottom of the furnace. Again depending on the exact level of oxygen pressure the other heavy metals are more or less co-reduced with the iron and dissolve in the metallic

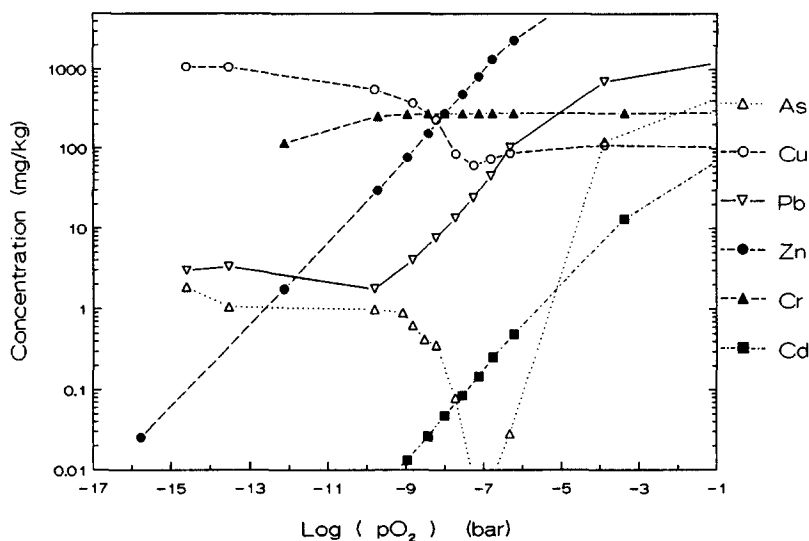


Fig. 4. Heavy metal concentration in slag phase vs. oxygen pressure for fly-ash melting at 1873°K.

phase. This is, for example, the case for Ni and Co. Chromium requires the most stringent reducing conditions and will probably be rather difficult to remove unless the process is carried out under rather extreme conditions in, for example, an arc furnace. On the other hand, it can be argued that the Cr remaining in the slag will be in the Cr(III) form, having a very low thermodynamic activity. Therefore there may be no environmental objection against leaving some of it in the slag as this would make the smelting operation easier. Another route would obviously be to treat waste streams with a significant amount of Cr separately.

The behaviour of As is remarkable as its concentration in the slag phase first decreases and then increases with decreasing oxygen pressure. This is due to the fact that at higher oxygen pressures As will be in the oxidic matrix as arsenate. At lower oxygen pressures As is reduced, forming Cu_3As , which, under circumstances, exhibit the tendency to remain in the slag. The minimum amount of As in the slag is expected around $p\text{O}_2 = 10^{-7}$ bar.

Since the oxygen pressure is a crucial process parameter, control of it is very important. This can be done by careful control of the air or oxygen supply. The reducing conditions required are reached by addition of coal. Dependent on the desired composition of the slag phase (i.e., the oxygen pressure) the required amount of coal is determined. Fig. 5 shows the theoretical energy need for the smelting of MSW incinerator fly ash at 1773 and 1873 K (including the addition of limestone and lime), as a function of the oxygen partial pressure. It can be seen clearly that the energy required increases sharply if low oxygen partial pressures ($< 10^{-8}$ bar) are to be reached due to on the one hand the heat requirement of the increasing amount of off-gas and on the other the energy required for the metal reduction.

A crucial element within the slag phase is the presence of sulphur (S). At sufficiently high oxygen pressures ($> 10^{-6}$ bar) S is oxidised to SO_2 . At lower oxygen pressures, however, S forms a sulphidic phase, known as matte, with some of the trace elements, primarily copper. At low amounts of matte this phase will probably remain dispersed in the

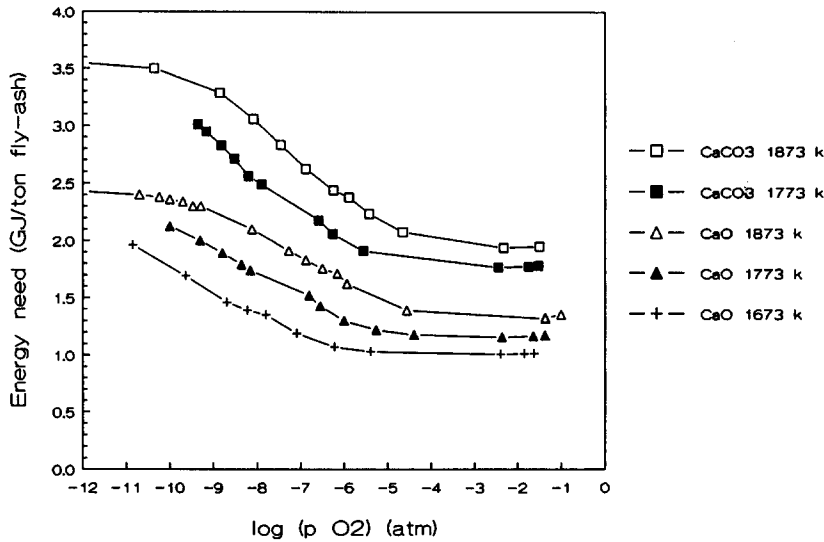


Fig. 5. Energy need (GJ/ton fly-ash) vs. oxygen pressure for the melting of fly-ash at 1773 and 1873°K.

slag phase thus increasing the amount of sulphur in the slag phase and an increased leachability, as this type of phases is known to be easily attacked and leached out of the slag matrix. At high S levels the matte can be expected to report as a separate liquid phase.

The slag bulk composition, i.e., the composition of the oxidic matrix, is hardly influenced by the oxygen pressure, as the bulk mainly consists of SiO_2 , CaO , Al_2O_3 and MgO . When P (e.g., in sewage sludge is present) it will also generally remain largely in the slag phase as $\text{Ca}_3(\text{PO}_4)_2$.

Table 2 shows the comparison of the calculated slag compositions with results of actual measurements performed by PBI (R. Bonn, personal communication). The measurements were taken during a pilot trial in a furnace having a capacity of approx. 1000 kg/h. The

Table 2
Measured vs. calculated values for fly-ash melting at 1873°K

Trace elements	Measurements (mg/kg)		Calculations (mg/kg)	
	input	output	$p\text{O}_2 = 10^{-8}$	$p\text{O}_2 = 10^{-11a}$
As	200	< 0.5	< 0.08	< 1.5
Cd	240	0.2	0.05	0
Cr	235	120	275	150
Cu	1070	79	86	7.6–650
Ni	70	6	18.3	3.9–5
Pb	5700	< 10	13.7	1–2
Zn	14 000	35	279	6
Sn	300	< 5	3.9	0.3
Cl	70 970	< 15	–	–
S	36 380	na	15 000	40 500

^aThe spread in concentration is caused by incorporation of the 'matte' phase in the slag phase.

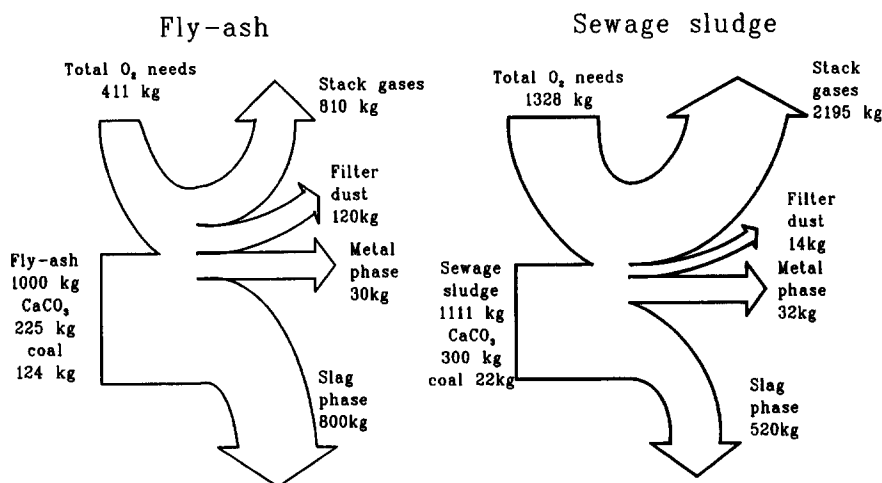


Fig. 6. Mass balance waster smelting process for fly-ash and sewage sludge at 1873°K.

measurements all fall within a certain range of oxygen pressures. Given the limited accuracy with which a representative concentration of trace elements within a bulk waste stream can be determined (especially due to the difficult sampling), the modelling can be seen to be quite acceptable as an indication of what will actually happen in a waste smelting furnace. The composition of the slag phase can be seen to match the requirements for use in construction or for the production of mineral fibers.

Based on the encouraging results of the thermodynamic modelling with the EQUIMET program, some mass and energy balance calculations were carried out using the BICEPS program.

Fig. 6 shows the results of the mass balance calculations for the smelting of MSW incinerator fly ash and sewage sludge at 1873 K according to the previously described process. The main difference between sewage sludge and incinerator fly-ash is the amount of organic compounds in sewage sludge (61%). This results in a much lower amount of slag phase produced, but a much larger stack gas amount. The smelting of sewage sludge needs no external energy, because use can be made of the high calorific value of the sewage sludge. No account was taken of heat losses, however.

Table 3 shows the energy requirements for both waste streams. Clearly it is shown that the sewage smelting process releases energy despite the high water content, which must be removed before smelting. The smelting of incinerator fly ash requires at least 2.0 GJ/ton fly ash. The total amount of coal (high volatile bituminous coal) needed is 124 kg/ton fly ash (to which 225 kg limestone are added (Fig. 6)). The amount of coal added is not determined by the energy need of the process, but by the required reducing circumstances: the required partial oxygen pressure in order to be able to remove the heavy metals (Cr, Ni, Mn) from the slag phase via a metallic phase.

The energy need of the process can be provided for by admixing waste streams with high calorific values like sewage sludge. This is possible, because the quality of the output streams of the smelting process is rather insensitive to changes in mineralogical composition of the feed. The ashes of the combustible waste streams added are also undergoing the

Table 3
Energy needs for the melting of fly-ash and sewage sludge Fig. 6

	Incinerator fly-ash (GJ/ton dry solids)	Sewage sludge ^a (GJ/ton dry solids)
Energy need		
Drying	–	4.1
Melting	2.0	– 5.1 ^b
Heat recovery		
Slag phase	1.8	0.9
After burner + gas phase	3.0	4.6

^aThermal drying from 30–90% dry solids.

^bEnergy release because of high organic content (61 wt%).

smelting process, which removes the heavy metals and incorporates the ash phase into the clean slag phase.

5. Conclusions

The proposed smelting process can be well described by the use of modelling, based on thermodynamic equilibrium calculations. This modelling can be a powerful tool for the design and operation of waste smelting processes, with which it is possible to convert heavy metals containing waste streams, like incinerator MSW fly ash, into a clean slag phase and heavy metal containing residues, which meet recycling requirements. Consequently hardly any solid waste is produced.

The energy need of the smelting process can be satisfied by mixing in a waste stream with a high calorific value, because waste smelting processes are rather insensitive to changes in mineralogical composition of the feed.

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