

# Stabilization/solidification of ashes in clays used in the manufacturing of ceramic bricks

This paper presents the results of the lixiviation of metals from different mixtures of fly and bottom ashes that have been stabilized and solidified in clays used in the manufacture of bricks. The ashes used for this study were obtained from a Hoffmann-type brick furnace adapted for the incineration of municipal solid waste during the manufacturing of ceramic bricks. The ashes were stabilized in clay in different proportions of clay : ash mix (99 : 1, 95 : 5, 90 : 10, 80 : 20 and 60 : 40). Such mixes were used to manufacture bricks that were calcined at a temperature ranging from 50 to 1100°C. The clay, ashes and manufactured bricks were characterized using X-ray diffraction, fluorescent X-ray, thermogravimetry, differential thermal analysis, atomic absorption spectroscopy and scanning electronic microscopy. In addition, toxicity characteristic leaching procedure lixiviation tests were performed according to the EPA 1311 method for the determination of heavy metals. The results showed an affinity between clay and ash, and also that the bricks manufactured with these mixtures present low lixiviation levels. The tests also showed the highest decrease in the concentration of arsenic, nickel, chromium, zinc and silver for 99 : 1 mixtures. The 95 : 5 mixture was found to be the most favourable for the stabilization (greater concentration decrease) of lead and cadmium. Selenium was the metal with the lowest concentration change whereas arsenic, nickel, chromium, zinc and cadmium showed the greatest concentration change in all mixtures, with the exception of cadmium in the mixture 99 : 1.

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## Introduction

The final disposal of solid residues is a critical environmental problem in most Latin American countries, while appropriate disposal methods are only available in certain major cities (La Grega *et al.* 1994). In rural areas, sanitary landfills are not even available and residue incineration is not considered feasible due to the high costs associated with the operation. In this study, the incineration of municipal solid waste

(MSW) during the manufacture of ceramic bricks (a process referred to hereafter as coincineration) in a brick furnace was used as an option for the thermal treatment of waste. The aim of this project was to evaluate the environmental and technical feasibility of adapting a Hoffmann-type brick furnace to coincinerate municipal solid wastes from urban areas with a population of less than 20 000 inhabitants (Tabio,

Colombia), in compliance with the local regulations on emissions and on the final disposal of the process waste. To achieve this objective, many environmental factors need to be considered to make this process feasible. One of them is the generation of waste by concentrating contaminants such as bottom and fly ashes that should be adequately neutralized or treated (Dijkstra *et al.* 2002). Therefore, the stabilization of such ashes in clays used in brick manufacturing was studied as an alternative method for their disposal.

The main components of the clays used in the brick industry are silica oxide, aluminium oxide, and aluminium silicates (Sun *et al.* 2001). These materials, behave as ionic exchangers, in a similar manner to zeolites (García *et al.* 1999). In addition, the ashes produced by incineration contain certain typical compounds that are also encountered in clays such as SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and CaO (Arvelakis *et al.* 2005), which facilitates their mixing compatibility. This affinity, coupled with the ionic exchange capacity, appears to be the critical factor in terms of allowing the encapsulation of ashes in clays during the burning stage of the brick-making process. Therefore, the ash encapsulation process may be considered as a solidification–stabilization process (Magalhaes *et al.* 2005).

Some processes that deal with hazardous residues of different origin such as, for example, the cement-process are known as ‘solidification–stabilization’ techniques. Several authors have studied such processes using a great variety of residues and matrixes. Albino *et al.* have worked with a large variety of heavy metals using Portland cement as an agglutinating agent. In fact, the cement industry has extensive experience in the application of such technologies (Albino *et al.* 1995).

Recently, Sun *et al.* have been using marine clays to stabilize residues in the catalytic hydrogenation process, such as Co/Mo/Al<sub>2</sub>O<sub>3</sub> and Ni/Mo/Al<sub>2</sub>O<sub>3</sub>, in the oil industry (Sun *et al.* 2001). The resulting material was used to manufacture bricks through vitrification. Based on the results of lixiviation tests, the authors propose a way to explain the stabilization process. This mechanism involves two phases: in the first phase, the clay forms a matrix around the metals and ‘encapsulates’ them. In the second phase, the heavy metals form chemical bonds with clay and therefore are ‘incorporated’ into the matrix. The authors found that such incorporation takes place at temperatures exceeding 1000°C.

This study shows the results of the encapsulation of bottom and fly ashes produced during the coincineration of MSW, in clay mixtures used in brick-making,

## Materials and methods

The solid waste from the municipality of Tabio, Colombia, was coincinerated in a Hoffman-type furnace during the industrial process in the brick-making facility ‘Los Quiroga’.

The MSW was characterized previously to the coincineration process in order to evaluate the capabilities of the Hoffmann kiln to be used as an incinerator with small impact on brick production.

The Hoffmann kiln technology was selected because of its simple characteristics of operation and design, and because it is a widely used technology in the brick-making industry in Colombia as well as in other third-world countries.

The principle of operation differs from any other drying/heating/burning processes in which the product moves around the heat source for transfer. This type of kiln operates with a moving flame front, which means that the combustion is moving linearly in one way to complete the process.

A typical Hoffman kiln is composed of seven major components for its operation as can be seen in Figure 1 and also in Figure 3 below.

1. *Ducts and valves.* These devices allow the regulation of the induced draught (negative pressure) according to the position of the flame front on the kiln. As the flame front advances the valves close and open following its path. This feature of the kiln operation enables the regulation of the induced draught through various valves varying the dimension of the exhaust ducts.
2. *Fuel dosifier.* In this case, a ‘Carbojet’ type dosifier (Figure 2) regulates the amount of coal needed for the continuous operation of the kiln. The action of a centrifugal turbine propels the pulverized coal through the fuel port located on top of the gallery. This device advances manually at a rate of 1 line every 50 to 60 min (approximately). This advance corresponds to the flame front advance velocity. The fuel is introduced, as shown in Figure 3, through the six feeder ports, four in the line and two ports one line in advance.
3. *Brick arrangement.* The disposition of the bricks enables a good heat distribution for optimum quality of the bricks as a final product. The brick arrangement is well designed to enable the fuel inlet (pulverized coal and MSW) through the four inlet ports located at the top of the galleries.
4. *Galleries.* Tunnel-like construction where the raw bricks are placed for the burning/cooking process.
5. *Fuel ports and doors.* Allow the mass flows of raw material and the air necessary for combustion for the process. Through the kiln doors, the bricks are loaded and withdrawn from the process and the bottom ashes are swept and collected. When the galleries are loaded and fired, these doors are sealed with cooked bricks, clay and paper. In Figure 1, the numerals correspond to each of the doors, twelve on each side of the kiln. The fuel ports are the holes through which the fuel is introduced to the process. Each of these openings on top of the gallery has its own

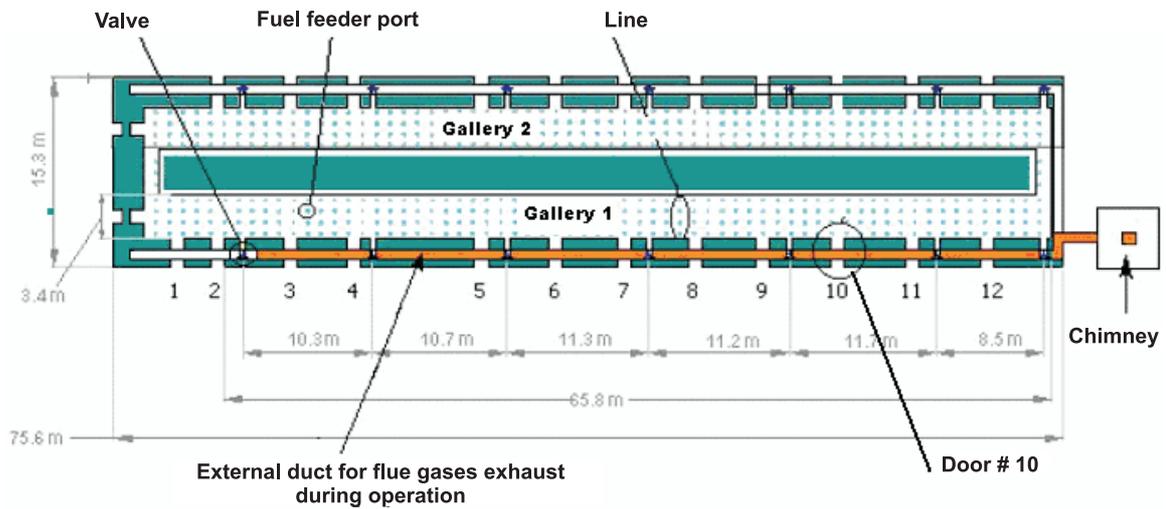


Fig. 1: Plant view and dimensions of the twin galleries symmetrical Hoffmann kiln, in the brick-making facility 'Los Quiroga'.

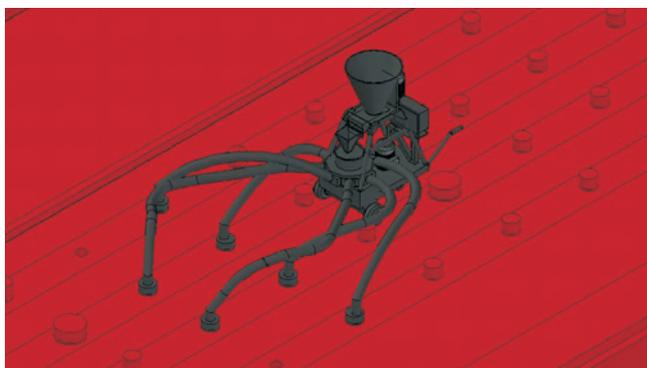


Fig. 2: 'Carbojet' type Fuel dosifier.

iron caps that are only uncovered to allow the fuel or MSW injection. The size of these opening is different as for coal the diameter is 10 cm and for MSW it is 30 cm. The distribution of the feeder ports is shown in Figure 3, where it can be observed that the MSW feeder ports are separated between each other by four lines.

6. *Paper barrier.* Needed to prevent the exhaust gases from filling the galleries completely, separating the ongoing process from the unburned batches inside the kiln. These paper barriers are burned when the flame front gets into proximity, permitting the next batch to enter the process and maintaining the continuous operation.
7. *Chimney stack and emissions control system.* Very important for inducing the air draught needed and exhausting the combustion gases.

The emissions evaluation of the kiln to be used as an incinerator involved both technical issues and environmental concerns.

Prior to the evaluation of the kiln, an emission control system with measuring instruments was installed on site. The system contributed to reduce the particulate matter (PM) and heavy metals emissions. The large-scale implementation weakness of the co-incineration process is the probability of formation of air contaminants, such as dioxins. Currently the temperatures achieved are between 900 and 1200°C distributed from the bottom to the top of the gallery. This aspect is important as the MSW incineration takes place at the bottom level of the gallery, and implies the need of a post-combustion chamber to achieve a homogenous temperature of the flue gases above 1200°C and enhance the residence time from 0.96 (estimated at 900°C) to 2 s. The post combustion chamber should be located along the exhaust ducts at the closest point to the front flame. Various configurations can be implemented.

The evaluation of the kiln, with a test batch of 2.5 tonnes of MSW per chamber (see Figure 6 below), showed that the fuel substitution (coal by MSW) was beneficial for reducing SO<sub>2</sub> (produced by the high sulphur content of coal) in the flue gases of the process, whereas other emissions (CO, CO<sub>2</sub>, NO<sub>x</sub>, HCl, HF, PM) remained fairly stable. In the measurement performed all contaminants, including dioxins and furans complied with the local regulation.

The Hoffmann kiln brick-making process presents several particular operational characteristics that are beneficial to the co-incineration of MSW and the encapsulation of ashes.

- The simple structural design and the common material used in the construction of the kiln.
- Low impact on the brick production process.
- This specific process is well known in the brick-manufacturing sector, increasing the number of specialized labour workers available in the market for working with this type of kiln.

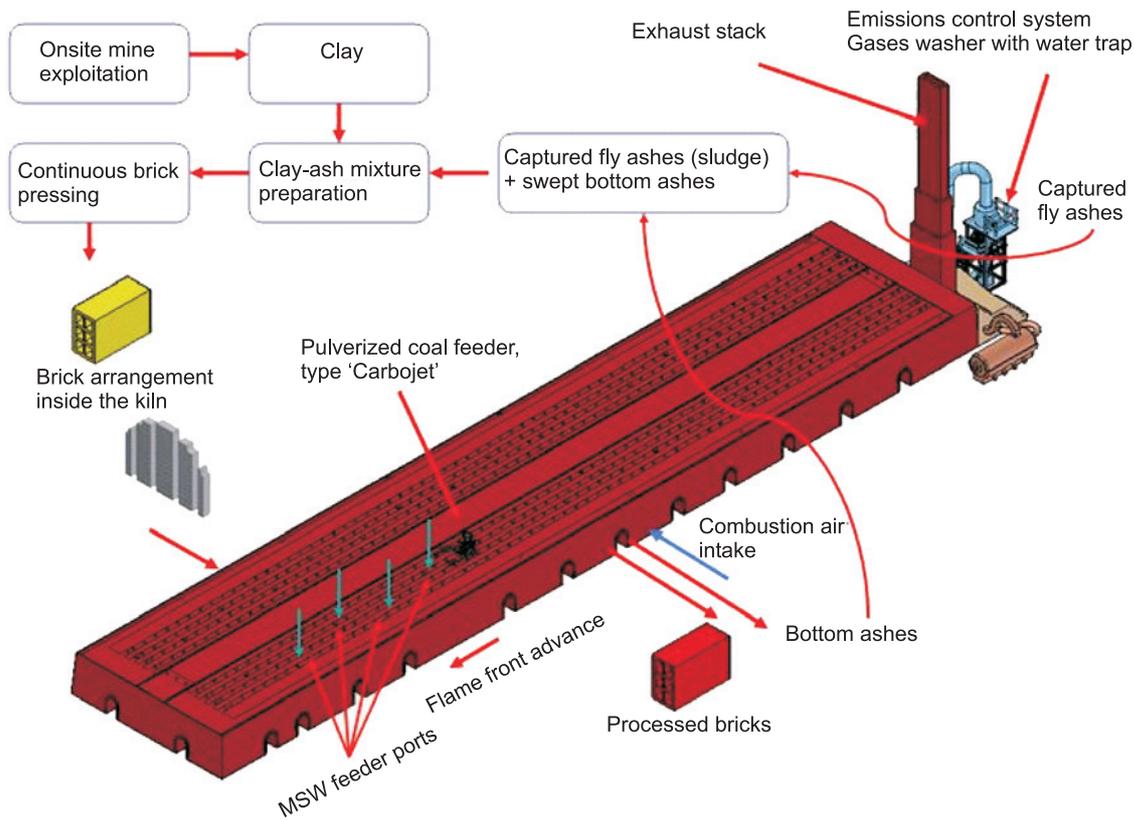


Fig. 3: Isometric view of the twin galleries symmetrical Hoffmann kiln, in the brick-making facility 'Los Quiroga'.

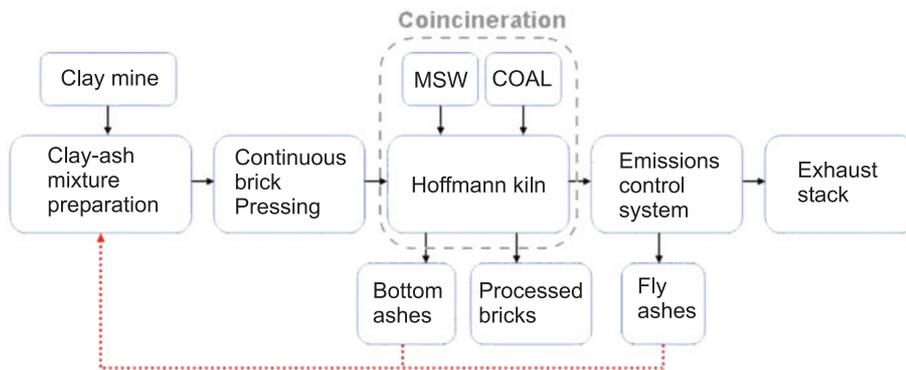


Fig. 4: Process flow of coincineration and encapsulation of ashes.

- Large amount of thermal mass helps maintain the temperature stable.
- Minimum of mobile parts and mechanical elements in the process hence simple operation.
- The present chimney stack could be elevated to higher altitude to increase draught and hence the turbulence.
- The emissions control equipment is sufficient to comply with the present local regulation on exhaust emissions.

The process flow of the coincineration is shown in Figure 4. The raw bricks access the kiln with average moisture (con-

tent of water) of 17%, through one of the opened doors. The doors are sealed and a newspaper barrier is constructed ahead of this batch inside the gallery. Once the flame front is close enough to burn the paper barrier, the flue gases circulate around the humid bricks, drying them. As the Carbojet approaches, the bricks are subjected to a slow preheating, due to circulating effect of the hotter flue gases. The preheating stage, prepares the bricks for the cooking, eliminating any residual moisture inside the clay, and reduces the probability of a thermal shock that could damage the product (Figure 5).

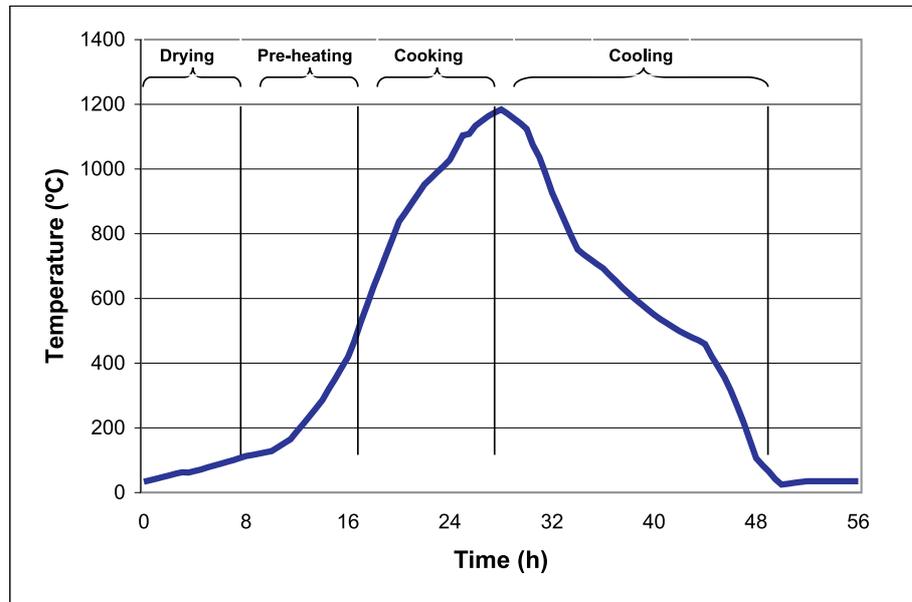


Fig. 5: Typical heating curve of Hoffmann kiln.

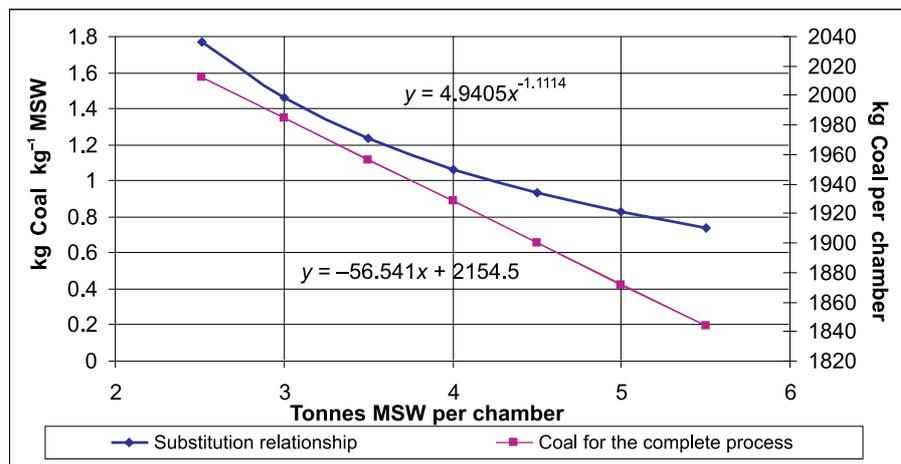


Fig. 6: Fuel substitution relationship.

At this stage MSW is added to the process, through bigger fuel feeder ports every four lines. The MSW is added as big bales of sorted residues. Since the temperature is considerably high, it has been established that a distance of four lines to the flame front is enough to completely dry the waste; the ignition takes place at the same moment as the fuel feeder is directly above the dried MSW. The MSW is sorted in order to take away the unburnable residues such as glass, metal and plastic bottles and large volume objects (see Figure 7 below). No shredding or screening is performed.

Once the flame front arrives at the preheated bricks, the temperature rises from 700 to 1200°C approximately, in a period of 6 h. Although the gases given off are passing through these hot zones, and since the emissions are kept within the

regulation limits, it must be assumed that the organic compounds are not being burned completely; that is the reason why a post-combustion chamber is recommended.

The coal substitution relationship was estimated from a heat balance and data acquired during the standard coincineration of 2.51 tonnes of MSW per chamber (one chamber is equivalent to eight lines). The coal used in the facility has a net calorific value of 33.1 MJ kg<sup>-1</sup> (Figure 6).

Once the flame has passed the cooked bricks, the incoming combustion air reduces the temperature of the bricks, to about 30°C and they are removed from the kiln, 24 h later, as a finished product ready to be sold.

The reduction in the fuel consumption as a function of the MSW introduced to the process can be attributed to the

Table 1: Results of the physical characterization of the MSW of Tabio.

Physical characterization				
Density (kg m <sup>-3</sup> )	234			
Compound	Weight (kg)	Moisture (%)	Moisture (kg)	Dry base (kg)
Organic matter	53.5	63	33.7	19.8
Plastics and rubber	12.5	3.0	0.4	12.1
Fabrics	6.5	3.5	0.2	6.3
Paper and cardboard	24.5	4.5	1.1	23.4
Metals	0.5	0	0	0.5
Glass and ceramics	2.5	0	0	2.5
Total	100		35.4	64.6

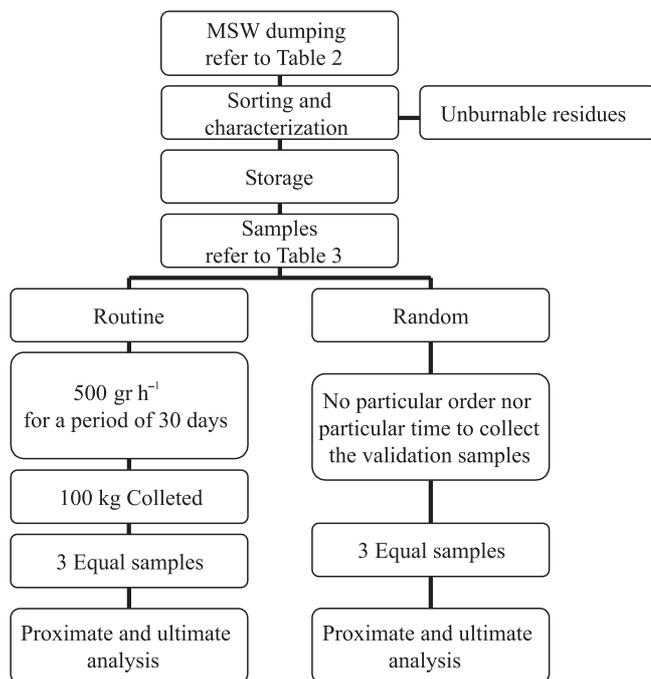


Fig. 7: Diagram of MSW sampling procedure.

fact that the advance velocity of the dosage device has to be increased to avoid overcooking of the bricks., Since the 'Carbojet' dosage device does not have any control to reduce the fuel injection, the total coal consumption is reduced this way

The ashes obtained from the MSW coincineration were analysed and mixed with the clays, with the aim of encapsulating the hazardous contaminants within the clay. The following heavy metals were studied specifically because of their impact on human health: arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), mercury (Hg), silver (Ag), lead (Pb) and selenium (Se) (Donnelly & Buonicore 1992).

The wastes were subject to proximal analysis and ultimate analysis according to the ASTM D3172 to D3175 method for the different waste bulks (each bulk weighed 2.5 tonnes) that were used for the coincineration tests. Each of the waste

Table 2: Fuel characteristics of the sorted MSW of Tabio.

Proximate analysis	
Net calorific value (MJ kg <sup>-1</sup> )	13.11
Water-content (%wt)	63.9
Ash-content (%wt)	3.3
Volatiles (%wt)	31.4
Fixed carbon (%wt)	1.3

bulks was subject to sorting and physical characterization (American Society for Testing and Materials 1983). The sampling procedure is shown in Figure 7, and the characterization results of the MSW and the sorted waste are presented in Tables 1 and 2.

For the characterization of the process clays, 500 g samples were collected every hour for 30 days at the plant. Once a total of 100 kg had been collected, three samples out of the total were selected and their elementary composition was determined using the following techniques: X-ray fluorescence (XRF) and X-ray diffraction (XRD), differential thermal analysis (DTA), atomic absorption spectroscopy (AAS), and scanning electronic microscopy (SEM). The laboratory analysis were carried out in the Laboratories of Porous Solids and Microcalorimetry of the Department of Chemistry of the University of Los Andes in Bogotá, Colombia, and in the Laboratory of Surface Sciences and Porous Media in the University of San Luis, Argentina, using the instruments listed in Table 3.

In addition to the collected samples, another three samples were randomly chosen on different days and at different times. Those samples were analyzed in the same way to validate the previously obtained results.

Bottom and fly ashes were collected during five coincineration tests. The fly ashes were collected at the emission control system which consists of a gas washer with a water absorption system.

The emissions control equipment enables the capture of 99.9% of the exhausted particles in the form of sludge. The

Table 3: Instruments used in the experimental measurements.

Analysis	Instrument	Model	Characteristics
XRD	RIGAKU	MINIFLEX	2–70° (c/0.02°), 2° min <sup>-1</sup>
XRF	PHILIPS	PW 1400	RXTube, RhAnode, HRcollimator
DTA	NETZSCH	STA 409 PC LUX	30–1100°C, 15° min <sup>-1</sup>
AAS	PERKIN ELMER	AANALYST 300	

sludge was mixed with the bottom ashes to prepare the clay–ash bricks mixtures. In order to characterize these mixtures, three samples were selected.

Their chemical composition was determined with the same techniques used with clays (XRF, XRD, DTA, AAS, and SEM). The remaining clay and ashes were used to prepare five mixes with the following proportions of clay : ash: 99 : 1, 95 : 5, 90 : 10, 80 : 20 and 60 : 40. Each mix was used to prepare 10 test bricks each weighing 200 g (Figure 8). These bricks were calcined in the laboratory, using a furnace of the commercial brand BARNSTEAD, Model 48000, following the typical temperature of the Hoffman furnace slope (Figure 5) as shown in Figure 9.

After the test bricks, that had been prepared with the different clay : ash proportions, were calcined in the laboratory, three tests bricks were chosen at random. In order to find the optimal clay : ash proportion, the selected bricks were characterized using the same techniques as previously applied to the clay and ashes. Finally, lixiviation tests were applied [toxicity characteristic leaching procedure (TCLP)]. The test consists mainly of a liquid–solid extracting action, allowing contact of the previously ground material ( $\leq 5\mu\text{m}$  particles) with aqua regia (mixture of nitric and hydrochloric acid). After several hours, the extract obtained is diluted and analysed with AAS for the different metallic compounds, according to the corresponding calibration curve of the instrument. The results of the lixiviation tests were compared with the initial concentrations of heavy metals in the ashes. The metal concentra-

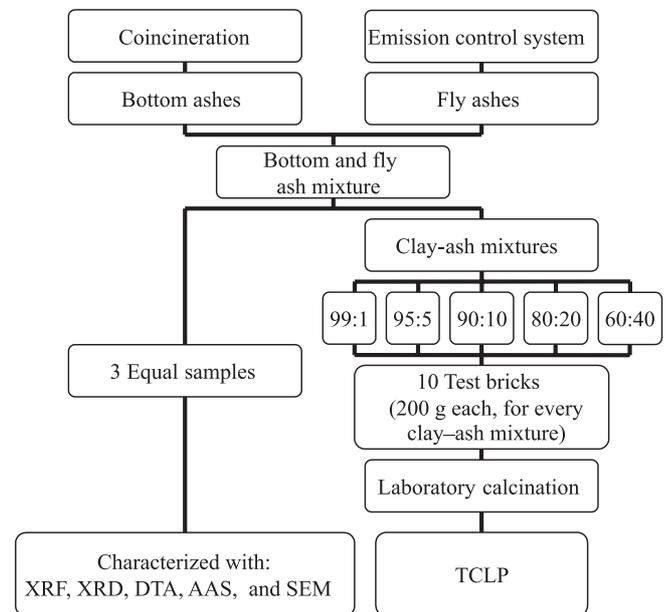


Fig. 8: Diagram showing the sampling procedure for the ashes and clay–ash mixtures.

tion change was calculated according to equation (1), in which the decrease in concentration is reflected as an increase in the concentration change rate.

$$\begin{aligned} & \% \text{ CONCENTRATION CHANGE} \\ & = \frac{C_{\text{Ashes}} - C_{\text{Bricks}}}{C_{\text{Ashes}}} \end{aligned} \quad (1)$$

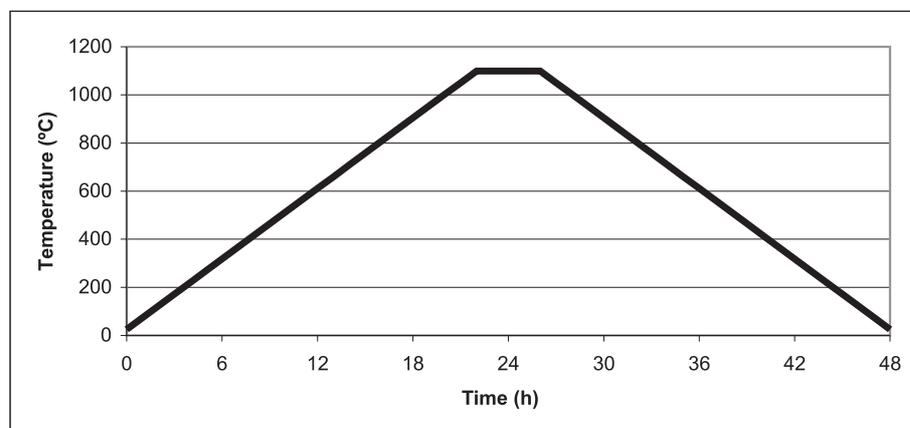


Fig. 9: Laboratory heating slope.

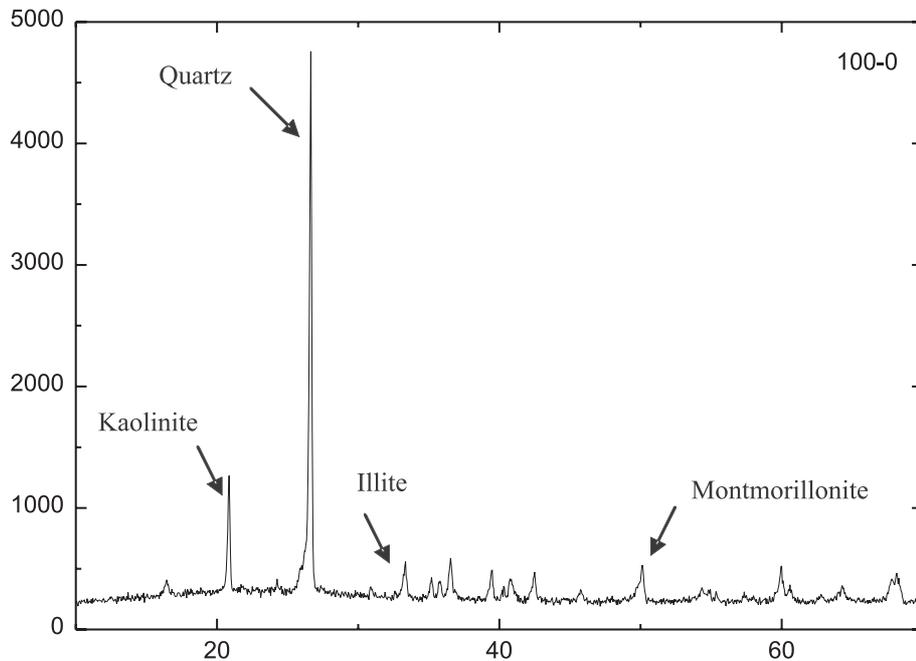


Fig. 10: Diffractogram of the Colombian clay used for brick production.

where  $C_{Ashes}$  is the initial concentration of metal in pure ashes before the stabilization process ( $\text{mg kg}^{-1}$ );  $C_{Bricks}$  is the concentration result obtained from the TCLP lixiviation test ( $\text{mg kg}^{-1}$ )

The concentrations were obtained from the lixiviation test. The units were normalized to  $\text{mg kg}^{-1}$ .

## Results

### Characterization of the municipal solid wastes

The results obtained in the physical characterization and the proximate and ultimate analyses of the MSW of Tabio, Colombia, are shown in Tables 1 and 2.

The reported values of the characterization as a fuel (Table 2) correspond to the sorted MSW. As previously mentioned and given that no shredding was performed, the sorting procedure was carried out to eliminate large chunks of unburnable residues such as plastic, glass or metal containers, that otherwise would make the process of feeding the MSW to the kiln and the total incineration of the remaining residues difficult. The proximate analysis values in Table 2 are reported from the laboratory testing.

### Analysis of clay and ashes

Figure 10 shows a diffractogram obtained by X-ray diffraction analysis of the Colombian clay used for brick production. Kaolinite, illite, montmorillonite and quartz were the main clay minerals.

The results of the analysis of the clay used and the ashes obtained from the coincineration of the MSW, using XRF

Table 4: Characterization of ashes and clay: XRF and TG characterization of the used clay (raw material) and the bottom and fly ash mix resulting from the coincineration of MSW.

Substance	Clay (%)	Ashes (%)
SiO <sub>2</sub>	58.5	41
Al <sub>2</sub> O <sub>3</sub>	24.7	16
CaO	0.5	12.5
MgO	0.3	2.5
Fe <sub>2</sub> O <sub>3</sub>	4.8	8.6
P <sub>2</sub> O <sub>5</sub>	0.5	8.4
N <sub>2</sub> O <sub>5</sub>	–	3.5
CaCO <sub>3</sub>	–	2.5
K <sub>2</sub> O	1.5	0.8
MnO	0.8	0.7
TiO <sub>2</sub>	0.9	1.1
Fe <sub>2</sub> SiO <sub>4</sub>	–	0.4
Moisture	7.5	–

and TG are given in Table 4. These results show the similarity between clay and ashes, in terms of high content of inorganic matter, specifically, the oxides from different metals.

The elementary analysis of the ashes shows that the concentrations were below the maximum level acceptable in the lixiviation tests for all the metals studied. These results are given in Table 5.

### Results of the lixiviation tests in the sample bricks

Although the initial analysis of the ashes shows that the typical concentration of ashes are below the acceptable limits

Table 5: Heavy metal contents present in the ashes: heavy metal concentration ( $\text{mg kg}^{-1}$ ) in ashes obtained from the MSW coincineration determined by lixiviation test.

Metal	Concentration	
	Ashes ( $\text{mg kg}^{-1}$ )	Maximum quantity accepted in lixiviation tests ( $\text{mg kg}^{-1}$ )
Arsenics (As)	1.12	5
Barium (Ba)	2.26	100
Cadmium (Cd)	0.43	1
Total chromium(Cr)	3.45	5
Copper (Cu)	1.56	
Mercury (Hg)	0.023	0.2
Magnesium (Mg)	4.72	
Nickel (Ni)	3.37	
Lead (Pb)	1.23	5
Silver (Ag)	0.083	5
Selenium (Se)	0.021	1
Zinc (Zn)	2.27	

for all the metals, the results of the lixiviation tests showed a significant reduction of the heavy metal contents in the clay-

ash mixes. Table 6 summarizes the results of the lixiviation tests according to the clay : ash proportions used. These results are shown in Figure 11.

The reduction percentage rate presented in Table 6 was calculated according to equation (1). From these results, the following observations can be made.

With the exception of silver, the reduction rate decreased with the increase of the ash content in the mixes. In fact, the concentration of heavy metals dropped when the ash content was higher than 10%.

When the ash content changed from 1 to 5%, the concentration change of Se, Cd and Pb increased. For Pb, the concentration change increased from 83.74 to 98.08% with 1 and 5 % of ash, respectively. The ash effect on Cd was greater; the percentage concentration changed from 53.49 with 1% of ash to 93.33% with 5% ash. The results of the lixiviation tests with the analysed metals for the test bricks manufactured with different mixes are shown in Table 6.

The above-mentioned results imply an uneven dilution of the clay-ash for the low ash content mixtures.

In the case of silver, the reduction was greater for the clay-ash mixes with 80 : 20 proportion than for the 90 : 10 proportions.

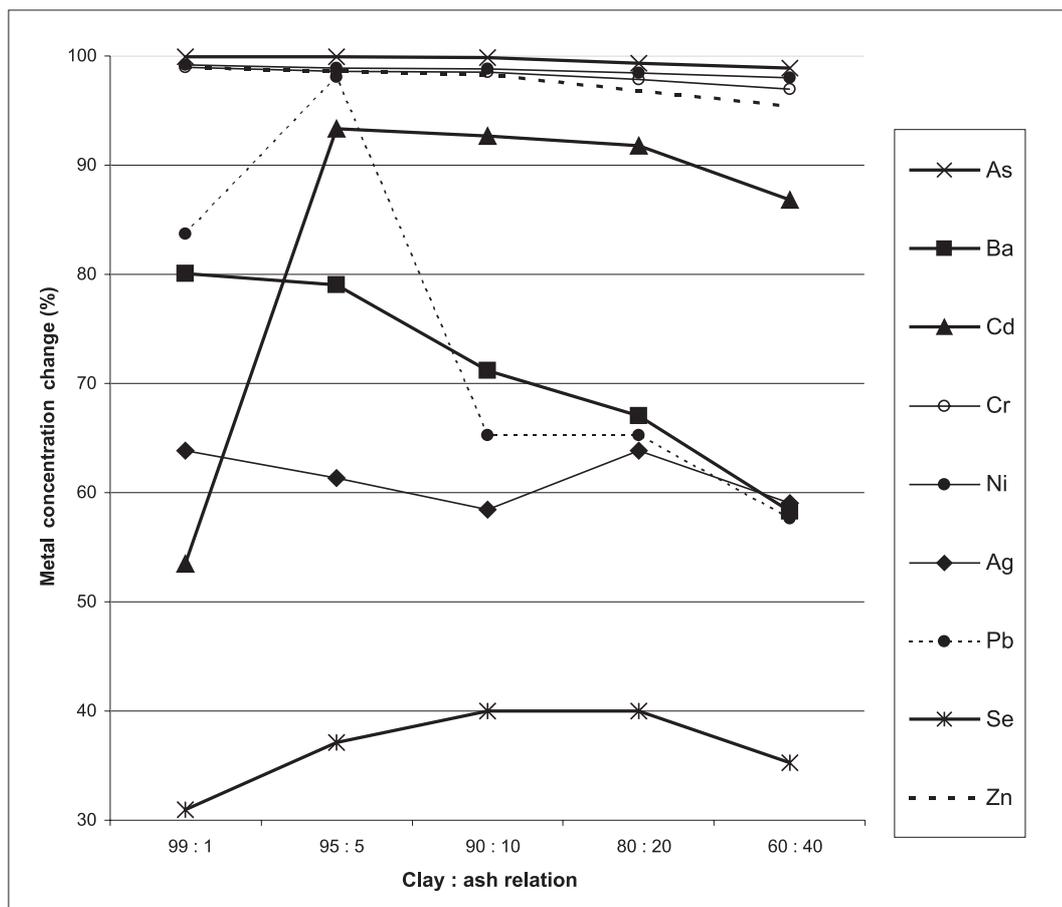


Fig. 11: Metal concentration change TCLP tests for five different samples of clay-ash mixtures.

Table 6: Results of the lixiviation tests in the test bricks: Heavy metal content in bricks manufactured with clay and ashes mixes in the incineration of MSW in Colombia.

Clay : ash weight		99 : 1	95 : 5	90 : 10	80 : 20	60 : 40
<b>Arsenic (As)</b>						
TCLP result ( $C_{Bricks}$ )	mg kg <sup>-1</sup>	0.001	0.0012	0.002	0.0076	0.0124
Pure ash concentration ( $C_{Pure\ ashes}$ )		1.12	1.12	1.12	1.12	1.12
% Concentration change	%	99.91	99.89	99.82	99.32	98.89
<b>Barium (Ba)</b>						
TCLP result ( $C_{Bricks}$ )	mg kg <sup>-1</sup>	0.451	0.474	0.652	0.745	0.9425
Pure ash concentration ( $C_{Pure\ ashes}$ )		2.26	2.26	2.26	2.26	2.26
% Concentration change	%	80.04	79.03	71.15	67.04	58.3
<b>Cadmium (Cd)</b>						
TCLP result ( $C_{Bricks}$ )	mg kg <sup>-1</sup>	0.2	0.0287	0.0314	0.0354	0.0568
Pure ash concentration ( $C_{Pure\ ashes}$ )		0.43	0.43	0.43	0.43	0.43
% Concentration change	%	53.49	93.33	92.7	91.77	86.79
<b>Total Chromium (Cr)</b>						
TCLP result ( $C_{Bricks}$ )	mg kg <sup>-1</sup>	0.0356	0.0479	0.0502	0.0738	0.104
Pure ash concentration ( $C_{Pure\ ashes}$ )		3.45	3.45	3.45	3.45	3.45
% Concentration change	%	98.97	98.61	98.54	97.86	96.99
<b>Mercury (Hg)</b>						
TCLP result ( $C_{Bricks}$ )	mg kg <sup>-1</sup>	ND**	ND**	ND**	ND**	ND**
Pure ash concentration ( $C_{Pure\ ashes}$ )		0.023	0.023	0.023	0.023	0.023
% Concentration change	%	> 56.5	> 56.5	> 56.5	> 56.5	> 56.5
<b>Nickel (Ni)</b>						
TCLP result ( $C_{Bricks}$ )	mg kg <sup>-1</sup>	0.027	0.038	0.041	0.052	0.067
Pure ash concentration ( $C_{Pure\ ashes}$ )		3.37	3.37	3.37	3.37	3.37
% Concentration change	%	99.2	98.87	98.78	98.46	98.01
<b>Silver (Ag)</b>						
TCLP result ( $C_{Bricks}$ )	mg kg <sup>-1</sup>	0.03	0.0321	0.0345	0.03	0.034
Pure ash concentration ( $C_{Pure\ ashes}$ )		0.083	0.083	0.083	0.083	0.083
% Concentration change	%	63.86	61.33	58.43	63.86	59.04
<b>Lead (Pb)</b>						
TCLP result ( $C_{Bricks}$ )	mg kg <sup>-1</sup>	0.2	0.0236	0.427	0.427	0.521
Pure ash concentration ( $C_{Pure\ ashes}$ )		1.23	1.23	1.23	1.23	1.23
% Concentration change	%	83.74	98.08	65.28	65.28	57.64
<b>Selenium (Se)</b>						
TCLP result ( $C_{Bricks}$ )	mg kg <sup>-1</sup>	0.0145	0.0132	0.0126	0.0126	0.0136
Pure ash concentration ( $C_{Pure\ ashes}$ )		0.021	0.021	0.021	0.021	0.021
% Concentration change	%	30.95	37.14	40	40	35.24
<b>Zinc (Zn)</b>						
TCLP result ( $C_{Bricks}$ )	mg kg <sup>-1</sup>	0.023	0.0326	0.0387	0.0723	0.104
Pure ash concentration ( $C_{Pure\ ashes}$ )		2.27	2.27	2.27	2.27	2.27
% Concentration change	%	98.99	98.56	98.3	96.81	95.42

\*The detection limit for the spectrophotometer is 0.1 ppm. Mercury samples were concentrated 10 times and mercury presence was not detected. The mercury concentration in the bricks ( $C_{Bricks}$ ) therefore was set to be < 0.01 mg kg<sup>-1</sup>.

\*\* Not detected.

## Conclusions

Although the concentration of heavy metals in non-treated ashes was below the acceptable limits, the results of the lixiv-

iation tests show significant reductions of these concentrations in the test bricks. The results of the lixiviation tests show that the metal content rate in the encapsulated ashes is between 30 and 99.9% lower than in untreated ashes.

A higher stabilization of the metal lixiviation in mixes with a clay : ash content of 99 : 1, 95 : 5 and 90 : 10, respectively, was observed, even though the lixiviation tests performed did not allow the optimal clay–ash mix to be determined.

Generally speaking, the levels of removal and encapsulation are considerably greater for arsenic, nickel, chrome, zinc and cadmium (except for 99 : 1 mixes).

Selenium revealed lower rates of removal and encapsulation. Silver, barium and lead showed intermediate levels depending on the mixture proportions.

The predominant composition of kaolinite in the used clay and the presence of metallic oxides in the ashes leads to the assumption that the formation of spinel may be among the mechanisms that allow the stabilization of the present metals, given that the temperature of the brick-making proc-

ess reaches 1100°C (Lingling *et al.* 2005). As is well known, the spinel is a very stable and chemically inert crystalline phase that may congregate a large quantity of metallic oxides in the aluminosilicate structure (Okada *et al.* 1986).

The effect of the mechanical properties and final quality of the bricks manufactured with clay–ash mixtures should be addressed in order to validated the large-scale implementation of the results here exposed. It is especially recommended to investigate these effects on the high ash content mixtures.

Another possible stabilization process that may be taking place in the clay–ash mixes during the brick-making process is the formation of vitreous phases, especially by oxidation–reduction reactions; by the loss of humidity, and by the cationic exchange occurring when the brick-making temperatures exceed 1000°C.

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