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SPECIAL ISSUE

Environmental suitability of ceramic raw materials: a geochemical approach to volatile emissions and leaching potentials

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Abstract Growing environmental concern is promoting the necessity of additional ceramic tests. The use of unknown materials with potential contamination conditions requires further studies to demonstrate that the piece encapsulates the pollutant and that during its firing it does not produce the emission of harmful volatile elements. The objective of this work was to perform both tests in a ceramic paste made with slip-casting wastes and electroplating residues. The leaching methods for determining the encapsulation of potential harmful elements were performed following the TCLP, EP-Tox norm. Having precise chemical analysis of both crude and fired brick, the problem of emissions losses during the firing can be solved by the gain/loss techniques used in geological studies. In particular, the Isocon method that permits a quick visualization of the lost elements is useful. Once the volatile elements were determined, their amount was calculated considering a constant element and the chemical concentrations normalized by the loss of ignition, or using the crude/fired brick ratio densities. The leaching tests indicate that the ceramic brick does not produce harmful leachates according to Argentinean specifications. The leachates of B and Ca are high. Ca does not seem to be a problem while

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Piedra Grande SA, Dique Florentino Ameghino, Dto. Gaiman, A.P. Bell 569, 9100 Trelew, Argentina the B content is beyond the permitted limits. During the firing, volatilized elements are Ag, Br, Cl, F, Hg, S, Se, and H₂O. The loss of Ag, Br, and Se are negligible. For F and Cl the potential emission rate is very low (100 mg/kg) while in the case of S, the 2,600 mg/kg rate is high. However, extrapolated emission rates at the chimney assuming an air-to-brick ratio of 2.5 N m³/kg, are approximately 1,040 mg/N m³ for S and 40 mg/N m³ for F and Cl, falling inside environmentally acceptable values. The geochemical procedures proved to be useful tools to assess the element mobilization during firing of ceramic wares and in the analyzed case, the results indicate that the paste is environmentally acceptable.

Keywords Clay brick · Volatile emissions · Galvanizing sludge · Waste recycling · Leaching behavior

Introduction

The increasing environmental concerns require that new ceramic formulations be tested before their utilization in industrial processes. In the traditional ceramic plants, several laboratory tests are usually carried out before accepting a new raw material. These tests incude measuring physical and chemical characteristics of clay bodies, as well as their responses during the ceramic process (Murray 2007). However, the use of unknown raw materials involves potential contamination, especially in the case of industrial by-products and residues, which requires a preliminary assessment to prove that the ceramic body actually incorporates the pollutant and that no harmful elements are released as volatile emissions during processing (Dondi et al. 2002; Galán et al. 2002; Xie et al. 2003; Cusidó et al.

2003; García-Ten et al. 2006) and/or as leachate from the finished product (Domínguez and Ullmann 1996; Cheesman et al. 2003; García Ubaque et al. 2007; Chiang et al. 2008; Lafhaj et al. 2008).

Emission rates of the industrial plants are usually measured by sampling the flue gas at the kiln chimney. However, any non-compliance with environmental rules and regulations may have serious legal repercussions, including mandatory interruption of production, so it would be most useful to have a suitable method to reliably predict volatile emissions during firing. If standard laboratory protocols are not available, accurate chemical analyses of both unfired and fired bodies can help to predict such emissions. The loss of volatile elements during firing can be expressed as the potential emission rate, i.e. the maximum value attainable if the amount of a given volatilized element is entirely drifted away to the chimney (Fabbri and Dondi 1995; González et al. 2002, 2006). This method needs to account for the overall weight loss during firing, which can be alternatively done using the density ratio of unfired/fired bodies. At any rate, the problem of volatile emissions during firing can be addressed by a geochemical approach, through the gain/loss techniques used in geological studies on metasomatism and hydrothermal alteration (Lindgren 1900; Domínguez and Ullmann 1996). In particular, the Isocon method allows a quick visualization of element losses (Gresens 1967; Grant 1986; Guo et al. 2009).

Leaching methods for determining the potential environmental risk are performed by many procedures, e.g. following the TCLP, EP-Tox test (US-EPA 1986).

In the ceramic tile industry, fluorine, chlorine and sulfur emissions have been monitored and regulated since the 1970s (Bonvicini et al. 2006). In the brick production, a summary of F, Cl, and S release was published by Fabbri and Dondi (1995) and references therein, and recent advancements have been discussed by González et al. (2002, 2006). An important aspect is that some components of the ceramic body, such as calcium carbonate, may contribute in fixing parts of S, Cl and F (perhaps other elements as well) during firing, thus avoiding their release to the flue gas (Xie et al. 2003; González et al. 2006; García-Ten et al. 2006). On the other hand, little is known about the thermal stability of hazardous elements present in minor amounts in clay systems. Mobilization of Cr and V in clay bodies was investigated by Fabbri et al. (1989) and Dondi et al. (1997), but no systematic studies were undertaken, because of the strong dependence on each clay system.

The purpose of this work is to call attention on the usefulness of simple and cheap methods to characterize fired ceramic pieces as inert, even if the heavy metals are used in the glazes. Sometimes, ceramic wastes are listed as harmful under the suspicion that they could have leaching potential if used as a landfill material. Also, it is necessary to estimate the potential of hazardous gas emissions of unfired raw materials before considering a kiln installation. Methods used to test the potential leaching are standardized, while there is no generally accepted procedure to determine the potential of hazardous gas emission. In Argentina, more than 30,000,000 common bricks are annually produced in self-contained rudimentary kilns without any environmental control.

This work presents a geochemical approach to assess the environmental suitability of a brick made by mixing slipcast and electroplating waste with clays. The inertization of hazardous industrial waste into a ceramic matrix is widely pursued, being considered an environmentally acceptable solution (Domínguez and Ullmann 1996; Dondi et al. 1998, 2002; Cheesman et al. 2003; García Ubaque et al. 2007; Singh et al. 2007; Chiang et al. 2008; Lafhaj et al. 2008). However, caution is needed particularly in the case of products containing significant amounts of easily volatile or leachable elements.

Experimental

The brick was fired at around 920°C and had water absorption of 9.9 wt%. Both crude and fired brick (bulk density 1,726 kg/m⁻³ and 1,818 kg/m⁻³, respectively) were dry ground and pulverized for chemical analysis.

The leaching test was performed using the protocol of the US Environmental Protection Agency - EP Tox. (1986). A fired brick was previously crushed to obtain particles smaller than 9.5 mm in order to simulate the worst weathering conditions. Leaching was performed at 22 ± 1 °C for 24 h, stirring 10 g of the sample in 160 ml of double-distilled water. An aqueous acetic acid solution (0.5 N) was added, when necessary, to maintain the pH constant at 5 ± 0.2 . After extraction and filtration (filter paper with 0.45 mm pore size), the solution was made up to a final volume of 200 ml by adding double-distilled water. The chemical determinations were performed by ICP at the Argentinean Alexander Stewart Laboratories (Protocol M0720929).

In order to quantify the compounds volatilized during firing, chemical analyses (major, minor and trace elements) were performed by fused sample-inductively coupled plasma emission spectrometry (FUS-ICP), total acid digested sample-inductively coupled plasma emission (TD-ICP), instrumental neutron activation analysis (INAA), cold vapor Hg (FIMS) and infrared absortion leco (IR) according to the analyte searched at ACT LABS, Canada (Protocol A08-3775). The bulk density of crude bricks (ρ_u) and fired bricks (ρ_f) was determined as the weight/volume ratio at the UNSUR laboratories. The potential release of a given element during firing was evaluated as the difference in concentration (Δx) between crude (x_u) and fired (x_f) samples, following three different procedures:

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Table 1 Chemical analysis of (erude and fire	ed bricks											
Analyte symbol (unit symbol)	SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (T)	(%) Mn	O (%) N	AgO (%)	CaO (%)	Na ₂ O (%)	K20 (%)	TiO ₂ (%) P ₂ O ₅ (%)	LOI (%)	Total (%)
Detection limit Analysis method Crude brick	0.01 FUS-ICP 74.8	0.01 FUS-ICP 11.28	0.01 FUS-ICP 3.14	0.0 FU 0.0	01 01 0 S-ICP F 27 0	.01 US-ICP .4	0.01 FUS-ICP 3.03	0.01 FUS-ICP 0.66	0.01 FUS-ICF 1.63	0.001 FUS-ICF 0.375	0.01 • FUS-ICP 0.13	FUS-ICP 0.21	0.01 FUS-ICP 95.7
Fired brick Analyte symbol (unit symbol)	00.01 Bi (ppm)	Br (ppm)	2.08 Cd (ppm)	Co (ppm)	LI U Cr (ppi	n) Cs (p	22 pm) Cu (j	veru (mqq	1.44 H (dpd) H	A (mqq) t	0.11 g (ppm)	Mo (ppm)	(mqq) iN
Detection limit Analysis method Crude brick Fired brick	2 TD-ICP 2 2	0.5 INAA <0.5 1.1	0.5 TD-ICP <0.5 <0.5	0.1 INAA 137 121	0.5 INAA 4,210 3,430	0.2 INAA 4.1 3.5	1 TD-I 676 593	1 CP IN 29 26	AA IN <	AA IP	5 IAA/TD-ICP 1 6	2 TD-ICP 5 3	1 TD-ICP 439 383
Analyte symbol (unit symbol)	Se (ppm)	Sr (ppm)	As (ppm)	Th (ppm)	U (ppm)	V (ppm)	(mqq) W	Ba (ppn	udd) uZ (t	(6	Zr (ppm)	La (ppm)	Ce (ppm)
Detection limit Analysis method Crude brick Fired brick	0.5 INAA <0.5 2	2 FUS-ICP 426 375	1 INAA 27 17	0.1 INAA 11.3 7.4	0.1 INAA 6.7 4.7	5 FUS-ICP 53 44	1 INAA 14 8	1 FUS-IC 7,402 6,608	1 P MULT 2,800 2,550	INAA/TD-IG	2 CP FUS-ICP 10,150 9,132	0.05 INAA 34.1 24.7	1 INAA 76 49
Analyte symbol (unit symbol)	Be (ppm)	Pb (ppm)	Rb (ppm) Cl (%) S (%)	F (%) Hg (ppb) Tc	tal S (%)	Sb (ppm)	Sc (ppm)	Eu (ppm)	Sm (ppm)
Detection limit Analysis method Crude brick Fired brick	1 FUS-ICP <1 <1	5 TD-ICP 121 104	10 INAA 80 60	0.01 INAA <0.01 0.02	0.001 TD-IC 0.022 0.214	0.01 P FUS- <0.0 0.02	5 ISE FIM 44 3,84	0.0.00)1)5 31	0.1 INAA 17.5 15.1	0.01 INAA 8.22 7.08	0.05 INAA 2.03 1.06	0.01 INAA 10.4 5.73
The element symbol, measurem	ent unit, ana	lytical metho	od, and detec	tion limit a	re shown i	n the table							

1. considering the alumina concentration constant before (x_u^{Al}) and after firing (x_f^{Al}) following the Isocon procedure (Grant 1986):

$$\Delta x'' = [(x_{\rm u} - x_{\rm f}) \times (x_{\rm f}^{\rm Al} / x_{\rm u}^{\rm Al})]/100$$

 correcting for the loss on ignition (L.o.I.) according to Fabbri and Dondi (1995), Galán and González (2002) and González et al. (2002, 2006):

$$\Delta x = [(x_{\rm u} - x_{\rm f}) \times (100 - \text{L.o.I.})]/100$$

3. correcting for the bulk density ratio (Lindgren 1900): $\Delta x' = [(x_u - x_f) \times (\rho_f / \rho_u)]/100.$

Results and discussion

Volatilized elements

The chemical compositions of crude and fired bricks are reported in Table 1. Most elements did not undergo any appreciable volatilization, being more concentrated in the fired ware due to the weight loss during firing. In particular, Al_2O_3 , SiO_2 , and TiO_2 were clearly immobile during firing as well as Fe, alkaline and alkaline-earth elements. The element losses are shown in the Isocon diagram (Fig. 1).

The potential releases expressed by three different methods used are listed in Table 2 and point out that volatilized elements are bromine, chlorine, fluorine, mercury, selenium, silver, sulfur, and water. Halogens and selenium were below the detection limit in the fired ware, so the extent of their release cannot be accurately predicted. Although its emissions were over 50%, the absolute values (~200 ppm for Cl and F, ~2 ppm for Br) were very low—even assuming that the whole amount goes to the chimney—and surely below the threshold limit for gaseous emissions. The Ag, Hg, Br and Se concentrations were

minimal and could only be detected by a high-sensitivity chemical analysis (they do not appear on a routine chemical analysis).

Sulfur, mercury and silver were partially released averaging 89, 98 and 18%, respectively (Table 2). The absolute value of S was close to 2,000 ppm, so attention should be paid to avoid exceeding the standard threshold. However, the behavior of sulfur during firing is complex, due to SO_2 - SO_3 equilibrium, interaction with clay bricks and refractory furniture, and deposition of sublimates in the pre-heating zone of the kiln. These phenomena are likely to involve volatilized trace elements that could be, e.g., entrapped in sublimates, therefore not reaching the chimney.

It is to a certain extent unexpected that elements such as Pb, Sb, As, Mo, Cu—which are known to be easily mobilized at high temperature—are substantially stable. The main reason may be the firing temperature (close to 920°C) and the high thermal gradient inside the bricks, making it probable that the core did not exceed 700–800°C. A further effect could be slow release kinetics through the small-sized porosity of bricks, implying low gas permeability (Dondi et al. 2003).

The prediction of gaseous emissions is a complex problem since many factors can influence the results. Among the most important are, the concentration of the element in the raw material, the thermal stability of minerals containing the element, the firing schedule (thermal gradient, maximum temperature, soaking time, fuel used), the kiln atmosphere (air-to-fuel ratio, oxygen partial pressure) and the reactions that occur during firing, and the occurrence of compounds (such as calcite) that seem to promote the fixation of S, Cl and F during the firing process (Xie et al. 2003; González et al. 2006; García-Ten et al. 2006). The F, S, and Cl potential release was compared with literature data (Fabbri and Dondi



Fig. 1 Isocon diagram comparing crude and fired bricks. The line joining SiO₂– Al₂O₃–TiO₂ is the best Isocon fit. Losses are plotted in the lower field. Major element data are plotted in % and minor element and traces in ppm

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Table 2 Losses during firing

Element	Raw	Fired	Released 1	Released 2	Released 3	Released % 1
Ag	2.6	2.1	0.7	0.34	0.4	27
Br	1.1	<0.5	0.64	0.6	0.95	58
Cl	200	<100	100	100	100	50
F	200	<100	100	100	100	50
H ₂ O	7,200	210	7,010	6,900	6,980	97
Se	2	<0.5	1.54	1.5	1.95	76
S*	2,140	22	1,900	1,920	1,900	89
S ^p	3,100	500	2,600	2,600	2,600	85
Hg*	2	<1	1.08	1	0.95	54
Hg ^p	3.9	0.044	3.8	3.8	3.8	99

Values are given in ppm = mg/kg. S and Hg were determined by two different methods with different detection limits

Released 1, considering constant Al_2O_3

Released 2, considering ignition loss

Released 3, considering specific gravities

Released % losses using alumina constant

S^p: IR; Hg^p: FIMS; *S: TD-ICP, *Hg: INAA

Table 3 Fired brick TCLOP chemical leachate

Sample	Ag	Al	As	В	Ba	Ca	Cd	Co	С	Cr		Cu	Fe	Hg	g	К	Li	Mg	Mn
LD ppm	0.007	0.02	0.035	0.003	0.001	0.007	0.001	0.0	002	0.00	4	0.003	0.004	0.0	01	0.15	0.00	2 0.02	0.001
LC ppm	0.021	0.06	0.105	0.009	0.003	0.021	0.003	3 0.0	006	0.01	2	0.01	0.012	0.0)3	0.45	0.01	0.06	0.003
Fired brick	ND	0.12	< 0.10	11.915	0.134	11.298	ND	0.0	015	0.01	6	0.12	0.183	NI	D	14.20	0.00	7 0.58	0.047
Dup	ND	0.11	< 0.10	11.842	0.134	11.032	ND	0.0	011	0.01	3	0.12	0.182	NI	D	14.18	0.01	0.57	0.046
Sample	Мо	Na	Ni	Р	Pb	Sb	Se	Si	Sn		Sr	Tł	n Ti		Tl		U	V	Zn
LD ppm	0.005	0.02	2 0.01	0.05	0.028	0.021	0.05	0.02	0.0)17	0.00	0.0	03 0.	002	0.0	027	0.15	0.003	0.002
LC ppm	0.015	0.06	6 0.03	0.15	0.084	0.063	0.15	0.06	0.0)51	0.00	0.0	0. 00	006	0.0	081	0.45	0.009	0.006
Fired brick	< 0.015	16.9	0.04	ND	< 0.03	ND	0.19	3.91	0.1	101	0.05	5 NI	D N	D	<(0.081	ND	ND	0.658
Dup	< 0.015	16.5	53 0.03	ND	< 0.03	ND	ND	3.86	NI)	0.05	5 NI	D N	D	N	D	ND	< 0.009	0.643

LD detection limit, LC quantification limit, Dup duplicate

1995; González et al. 2002, 2006). The F emission was of 100 mg/kg, this amount being in the lower reported levels. The Cl emission of 100 mg/kg was in a similar condition. In the case of S, the maximum emission amount was of 2,600 mg/kg and is the highest reported levels.

Since hazardous industrial emissions are measured on the chimney exhaust gases, the extrapolation of laboratory data is only possible under the assumption that the volume of air needed for firing a brick is between 2.5 and 5 N m³/ kg (Bouscaren 1993). Considering an air volume of 2.5 N m³/kg, the emission rates of 1,040 for S, and 40 for F and Cl fall within the reported amounts. It is concluded that in the present case, the emissions are minimal and environmentally acceptable.

Leaching

Leaching data are shown in Table 3.

The TCLP leaching tests indicate that for the most harmful elements no contamination would be produced considering the Argentinean regulations (Table 4). Only the Ca and B contents were high. Ca does not seem to be a problem, while B (11 ppm) exceeded the limits for aquatic life protection (0.7 ppm) and also for animal-drinkingwater quality (5 ppm). A reduction of B leaching must be

Table 4 Leachate chemical composition and Argentinean	Element (unit)	This work	LDL	QL	Thresholds for drinkable water		
regulatory limits					(1)	(2)	
Fable 4 Leachate chemical composition and Argentinean regulatory limits (1) According to the Argentinian food code (2) Guidelines for mining wate quality (Ley N° 24585) <i>ND</i> not detectable, <i>LDL</i> lower detection limit, <i>QL</i> quantitation	Al (mg/L)	0.12	0.02	0.06	0.2	0.2	
	Ag (mg/L)	ND	0.007	0.021			
	As (mg/L)	< 0.105	0.035	0.105	0.01	0.05	
	B (mg/L)	11.915	0.003	0.009	0.5		
	Ba (mg/L)	0.134	0.001	0.003		1	
	Ca (mg/L)	11.298	0.007	0.021			
	Cd (mg/L)	ND	0.001	0.003	0.005	0.005	
	Co (mg/L)	0.011	0.002	0.006			
	Cr (mg/L)	0.016	0.004	0.012	0.05	0.05	
	Cu (mg/L)	0.124	0.003	0.009	1.00	1	
	Fe (mg/L)	0.183	0.004	0.012	0.3		
	Hg (mg/L)	ND	0.01	0.03	0.001	0.001	
	K (mg/L)	14.20	0.15	0.45			
	Li (mg/L)	0.007	0.002	0.006			
	Mg (mg/L)	0.58	0.02	0.06			
	Mn (mg/L)	0.047	0.001	0.003	0.1		
	Mo (mg/L)	0.005	0.005	0.015			
	Na (mg/L)	0.02	0.02	0.06			
	Ni (mg/L)	0.01	0.01	0.03	0.02	0.025	
	P (mg/L)	0.05	0.05	0.15			
	Pb (mg/L)	0.028	0.028	0.084	0.05	0.05	
	Sb (mg/L)	0.021	0.021	0.063		0.01	
	Se (mg/L)	0.05	0.05	0.15	0.01	0.01	
	SiO ₂ (mg/L)	0.02	0.02	0.06			
	Sn (mg/L)	0.017	0.017	0.051			
	Sr (mg/L)	0.0003	0.0003	0.001			
(1) According to the	Ti (mg/L)	0.002	0.002	0.006			
Argentinian food code	Tl (mg/L)	0.002	0.027	0.081			
(2) Guidelines for mining water	Th (mg/L)	0.03	0.03	0.09			
quality (Ley N° 24585)	U (mg/L)	0.15	0.15	0.45			
ND not detectable, LDL lower	V (mg/L)	0.003	0.003	0.009			
detection limit, <i>QL</i> quantitation	Zn (mg/L)	0.002	0.002	0.006	5.0	5	

obtained. This would be reached by immersing the brick in a diluted acid solution after firing.

Conclusion

limit

The growing uses of innovative and traditional raw materials in the ceramic industry together with an increasing environmental regulations create the need for additional tests before the acceptance of a new ceramic paste.

The methods used in this work are simple and useful. The prediction of toxic leachates from fired ceramic products and gas emissions during their firing must be a normal procedure in any new paste formulation and the evaluation methods must be clearly stated by local regulatory agencies.

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The leaching methods for determining the encapsulation of potential harmful elements could be performed following the TCLP, EP-Tox procedures of the USA EPA.

This work presents a geochemical approach to assess volatile emissions. The losses during firing can be solved by the gain/loss techniques used in geological studies by Lindgren and Domínguez and Ullman. In particular, the Isocon method by Gresens and Grant is useful as it allows a quick visualization of the lost elements.

The leaching tests indicate that the waste-bearing brick does not release harmful leachates according to the Argentinean specifications, but for B, this problem can be overcome by immersing the bricks in a slightly acid water bath soon after firing.

The only elements released during firing are Ag, Br, Cl, F, Hg, S, and Se. The emissions of Ag, Br, Hg, and Se are negligible. For F and Cl the potential emission rate is very low (100 mg/kg), while in the case of S the 2,600 mg/kg rate is high. However, extrapolated emission rates at the chimney assuming an air-to-brick ratio of 2.5 Nm³/kg, are approximately 1,040 mg/Nm³ for S and 40 mg/Nm³ for F and Cl, falling within standard and environmentally acceptable values.

Geochemical procedures proved to be useful tools to assess element mobilization during firing of ceramic ware, and in the analyzed case, the results indicate that the paste is environmentally acceptable.

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