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Al-rich sludge treatments towards recycling

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Abstract

A treatment method towards recycling of Al-rich sludges to produce high-alumina refractory ceramics is proposed. These sludges are collected in wastewater treatment units of industrial plants dealing with anodising or surface coating processes. This industrial residue usually contains significant amounts of soluble salts such as Na, K, Mg, Ca and Al sulphates that make direct recycling problematic. The removal of these salts from the as-received sludges by washing is ineffective due to its gel-like consistency. The treatment consists of calcining and subsequent washing operations, followed by removal of sulphates by precipitation as $BaSO_4$. The treated sludges could then be well dispersed and processed by slip casting. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Al_2O_3; Sludge; Leaching; Recycling; Refractories; Slip casting

1. Introduction

Waste management is a very important issue both from the public health perspective, and the environmental and industrial view points, because an ever-increasing amount of inert or hazardous materials need to be disposed in a safe and economical way or, preferably, reused whenever possible. In fact, the residues produced by a given industry can often be regarded as useful raw materials for other industries, thus reducing the negative environmental impact associated with landfill and preserving non-renewable natural resources.

The aluminium industry is highly concerned with the huge amounts of Al-rich sludges that are produced annually and the problems related with waste management, storage and/or transportation costs for disposal. Only in EU countries, the amounts of Al-rich sludges produced every year were estimated to be about 100.000 metric tons.[1] After filter pressing, these sludges are basically constituted by water (up to ≈85 wt.%), colloidal aluminum hydroxides and soluble salts such as Na, K, Mg, Ca and Al sulphates.[2]

Some attempts have been made to incorporate this type of residue in several matrix materials, such as concrete, glass and ceramics, namely, heavy clay materials.[3–9]

However, the high water content and the gel-like consistency of sludges make hard the obtaining of homogeneous mixes with the other raw materials and increase the drying shrinkage of ceramic bodies. On the other hand, Al-rich sludge previously dried at 100 °C exhibits a strong agglomerated structure that also hinders a good mixing with the other raw materials to be achieved. A non-homogeneous mixing means that discrete un-reacted refractory portions of sludge will remain inside a low temperature maturing red-clay matrix. This explains the decreasing mechanical properties and the increasing water absorption values of the as fired products.[2,3]

More recent and successful recycling ways have been proposed for the Al-rich sludge, namely as the main compound in mullite or mullite–alumina formulations, taking advantage of the predictable high alumina contents in the calcined residues.[10,11] However, the presence of significant amounts of soluble salts brought about some difficulties in obtaining a proper dispersion. Accordingly, the slip casting bodies were less dense and less reliable compared with the ceramic products shaped by dry pressing or extrusion. Salts segregation and migration to the drying surfaces also occurred more extensively in the slip casting samples. These studies

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demonstrated that soluble salts in the sludge still remain a problem, especially for wet processing methods.[11] Furthermore, since the soluble salts are mainly sulphates, which will decompose on sintering releasing SO_x to the atmosphere, recycling of Al-rich sludges in ceramic matrixes would imply a suitable treatment.

The present work proposes a method for treating this type of residue involving calcination and successive washings for the removal of soluble salts. The sulphates can then be precipitated from the washing water as an almost insoluble product ($BaSO_4$), while the washed powders can be easily dispersed and used for producing high-alumina ceramics by slip casting.

2. Experimental procedure

2.1. Sludge characterisation

The residue used in this work comes from a waste-water treatment unit of an industrial plant (Hydro Building Systems, Pombal, PT) dealing with anodising or surface coating processes. The as received Al-rich sludge is amorphous and mostly constituted by aluminium hydroxide. Na, Ca, and Al sulphates are also present as minor constituents. Its moisture content determined on drying at 100 °C for 24 h, in four samples collected in different positions of the as-received wet material, varied in the range 80–85 wt.% (wet base). The elemental composition of dried sludges was performed by XRF (PW 1400 Philips, The Netherlands) and the results are presented in Table 1. The data in bold are the major elements. A more complete characterisation of this type of industrial residues has been already reported in previous works.[3,11,12]

2.2. Sludge treatments

The as-received sludge was first dried at 100 °C for 24 h and then calcined at different temperatures (500, 800 and 1400 °C) using a heating rate of 5 °C/min, 4 h holding at maximum temperatures, followed by natural cooling down inside the furnace. The weight losses were determined from the weight of the samples before and after the heat-treatments.

The dried and calcined materials were washed with distilled water at pH 4 to evaluate the influence of heat treatment on the removal of soluble salts. It is known that alumina and aluminium hydroxides develop a maximum zeta potential at ≈pH 4, far away from their isoelectric points situated at about pH 8–9.[13] The pH adjustment was done with a 1M HCl solution, an acid commonly used to electrostatically stabilise alumina suspensions.[14] The washing procedure consisted of dispersing about 20 vol.% solids (the maximum solids loading that could be obtained from the dried sludge) in distilled water at pH 4 by stirring the slurries for 20 min. The as prepared suspensions were then centrifuged at 5000 rpm for 10 min to separate solids from the liquid and decanted. This procedure was repeated four times, and the elemental concentrations of Na, K, Mg, Ca and Al in the supernatant liquid solutions (Table 1) were analysed by ICP spectroscopy (Model 70 Plus, Jobin Yvon, France). The concentrations of eluated sulphates (Table 1) were determined using a gravimetric

Table 1
Elemental analysis of the dried sludge and the evolution of the total concentration of some elements leached by washing with the temperature of heat-treatment

Element	Elemental concentrations (wt.%)				
		Leached after heat-treating the sludge at:[b]			
	Sludge dried at 100 °C[a]	100 °C	500 °C	800 °C	1400 °C
Na	**0.62**	0.184	0.4632	0.598	0.607
K	0.23	0.002	0.008	0.031	0.021
Mg	0.07	0.0168	0.0628	0.0636	0.03
Ca	**0.65**	0.093	0.57	0.59	0.43
Sn	0.30				
Al	**24.10**	0.426	0.776	1.176	0.46
Fe	0.41				
Cr	0.25				
Si	0.46				
Cl	0.15				
P	0.21				
S	**4.51**				
SO_4[c]	**13.50**	0.6896	5.59	12.8	9.49

[a] As determined by XRF analysis.
[b] As determined by ICP spectrometry analysis.
[c] Calculated based on the S content.

method,[15] i.e. by precipitating them as barium sulphate from acidified solutions, according to the following equation:

$$SO_4^{2-}{}_{(sol.)} + BaCl_2{}_{(sol.)} \rightarrow BaSO_4{}_{(s)} + 2Cl^-{}_{(sol.)} \qquad (1)$$

For sulphate analysis, a volume of 25 ml of supernatant solution was diluted to 50 ml with distilled water and the acidity set at pH 1 with 2M HCl solution, and then heated at 80 °C. Increasing amounts of a previously prepared solution of 1M $BaCl_2$, kept at 80 °C were then added to the sulphate containing solutions to precipitate all the SO_4^{2-} ions as $BaSO_4$. It could be concluded that, at least 15 ml of the $BaCl_2$ solution was required to accomplish precipitation from the first washing solution. This volume was, therefore, adopted in all cases. The precipitated $BaSO_4$ was then separated from the aqueous media by centrifugation and dried in an oven at 100 °C during 12 h, cooled at RT in a desiccator and weighed. The X-ray diffraction patterns of precipitated $BaSO_4$ powders were resolved by XRD, (Rigaku, Tokyo, Japan), using CuK_α radiation, at a scanning speed of 1° (2θ/min).

Particle size distributions of the sludge particles before and after washing were carried out with a Coulter CSL 230, (Oakley Court, UK). Before particle size measurements the samples were deagglomerated in a planetary mill for 2 h at 150 rpm.

2.3. Preparation, rheological characterisation and slip casting performance of slurries

The powders calcined at different temperatures and washed were individually dispersed in distilled water in the presence of a proper amount of a dispersant (Targon 1128, BK Landenburg, Landenburg, Germany). Slurries containing up to 40 vol.% solids could be easily prepared from the sludges calcined at 800 and 1400 °C by adding the powders to the aqueous dispersant solution under mechanical stirring for 20 min. Deagglomeration was performed by ball milling in a planetary mill for 2 h, keeping the acidity of the suspensions at pH ≈4. A de-airing step followed by rolling the suspensions in plastic containers without balls for 2 h.

Suspensions containing 30 vol.% of each treated solids were characterised by rheological measurements using a rotational controlled stress rheometer (Carri-Med 500 CSL, UK) with a cone and plate-measuring configuration. Before starting a measurement, pre-shearing was performed at high shear rate for 1 min followed by at rest of 1.50 min in order to transmit the same rheological history to the whole suspensions being tested.

Hollow shapes could also be prepared by slip casting. The green parts were sintered at 1600 °C for 2 h holding time, using a heating rate of 5 °C/min and free cooling down.

3. Results and discussion

3.1. Influence of sludge treatments on powders' characteristics and on the contents of soluble salts

As referred in the experimental part, the as-received and calcined (at different temperatures) sludges were successively washed and redispersed for four times. The aim was to evaluate the effects of the heat treatment temperature on the particle size distribution and on the leaching ability. Table 1 reports the elemental XRF analysis of the sludge dried at 100 °C and the evolution of the total concentration of some elements, leached by washing, with temperature of heat-treatment. It can be seen that Al is the most abundant element in the sludge, which also contains a significant amounts of S, Ca and Na, as well as minor amounts of the other elements. On the other hand, the amounts of some of these elements leached during washing increase with increasing the temperature of heat-treatment up to 800 °C, decreasing with temperature further increasing due thermal decompositions of the salts. Most of the sulphate species could be removed from the sample heat-treated at 800 °C, while the washing efficiency was still poor at 500 °C.

Fig. 1 shows the particle size distribution (PSD) of calcined powders before and after washing. No significant PSD differences can be observed between washed and non-washed powders calcined at 500 °C. Small differences are apparent between samples heat-treated at 800 °C, although without a clear trend (washing seems to have caused a decrease of the fraction of coarse agglometares, while tend to promote agglomeration of finer particles). Contrarily, a clear trend can be observed for samples calcined at 1400 °C, with the washed powder presenting a higher volume fraction of fine particles, as compared with non-washed one. This can be understood, since the removal of soluble salts will enable a better dispersion to be obtained. In fact, the soluble species will compress the electrical double

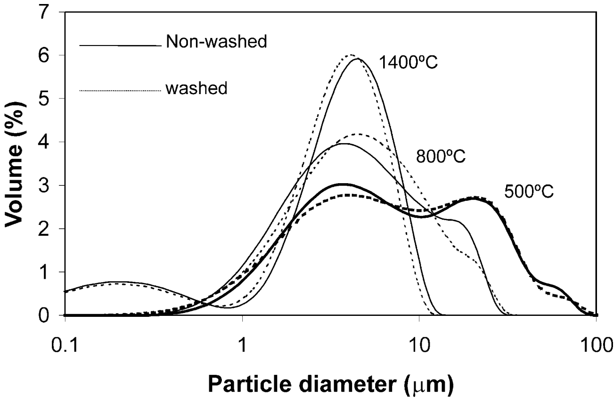

Fig. 1. Particle size distribution of the sludge calcined at 500, 800 and 1400 °C, before and after washing for four times.

layers decreasing the repulsive component of the interaction forces, according to the Derjaguin, Landau, Verwey and Overbeek (DLVO) theory.[16,17] On the other hand, it can be seen that the broadest PSD corresponds to the lower calcination temperature, where a population of particle agglomerates appears centred at about 20–30 μm. A narrowing trend is observed with increasing temperature with the narrowest PSD and the finest average particle size being obtained at 1400 °C. These differences might be due to the presence of hydroxyl groups and salts connecting the primary particles and leading to the formation of large agglomerates. The measured weight losses, calculated on a wet base, experienced by the dried sludge after heat treating for 4 h at 500, 800 and 1000 °C were 44, 49 and 52 wt.%, respectively. The weight losses at 500 °C and even at 800 °C might be mainly due to the release of hydration water and hydroxyl groups.[18] Based on these results and on elemental analysis (Table 1), one can conclude that the content of alumina in the fired products made from the Al-rich sludge is higher than 90%. In fact, XRD spectra (not shown) of the washed sludge calcined at 1400 °C revealed that alumina was the only crystalline phase detected. Decomposition of pure aluminium sulphate is predicted to start at 770 °C[19] and should therefore be already initiated at 800 °C, which will be completed up to 950 °C.[18,20] The presence of some Na and Ca sulphates in this type of sludges calcined at temperatures as high as 1400 °C has been claimed in previous works.[18,20] Although the results presented in Fig. 1 suggest that a more deagglomerated and better dispersible powder could be obtained at the highest

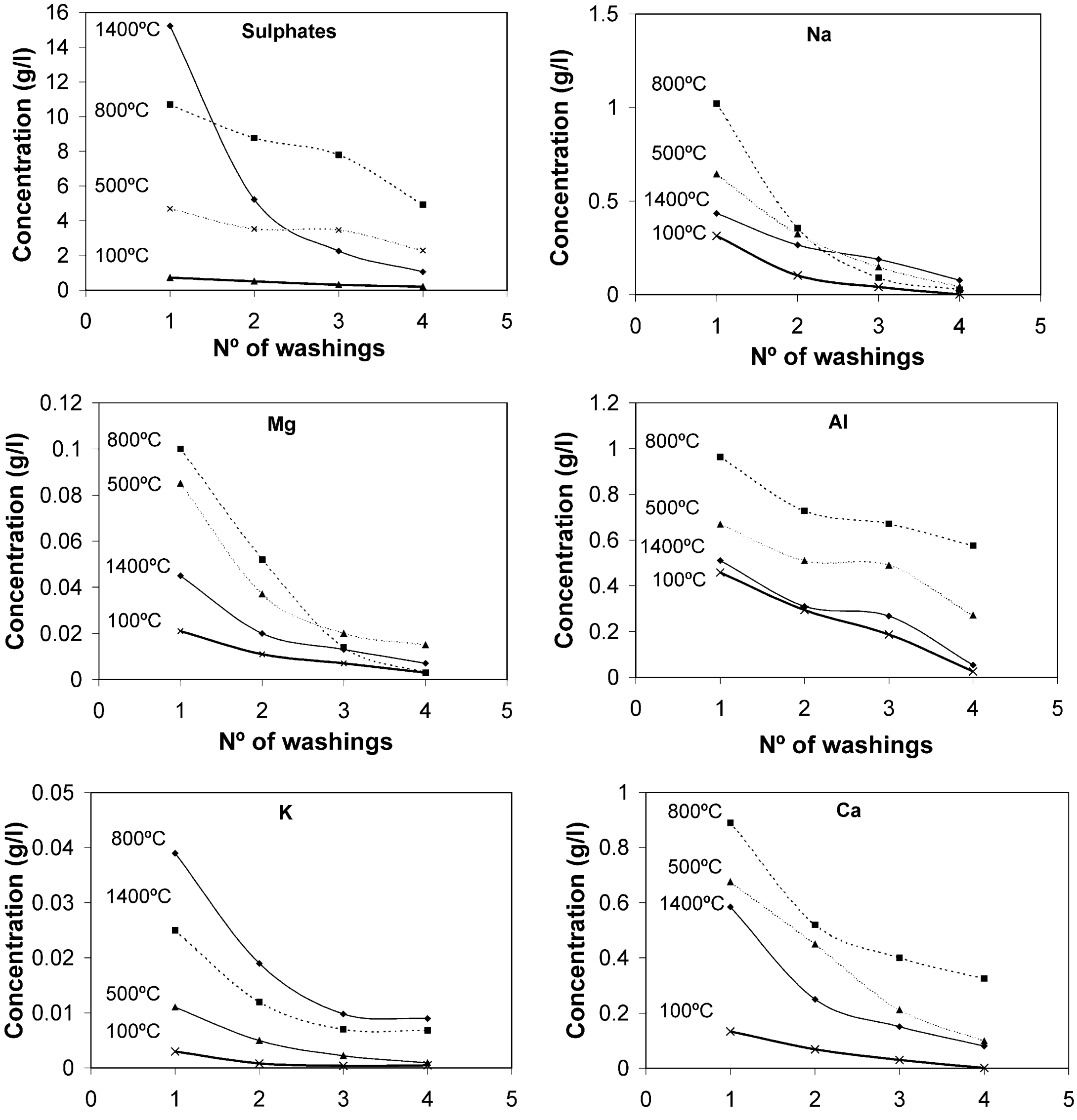

Fig. 2. Evolution of the concentration of soluble species in the supernatant solutions along the successive washings for the dried and calcined (at different temperatures) sludges.

calcination temperature, problems related with energy consumption and the release of dangerous gaseous species to the atmosphere desencourage such practices.

The concentrations of the main soluble species leached along the washing process are presented in Fig. 2, while their cumulative amounts are plotted in Fig. 3. It can be observed that the elution rate is generally higher from the sludge calcined at 1400 °C. These results are consistent with a less agglomerated powder (Fig. 1). Combining the information given in Figs. 2 and 3, one can conclude that, the cumulative amount of sulphates is maximum in the sludge calcined at 800 °C, and follows the order 800 °C > 1400 °C > 500 °C > 100 °C. For the other analysed species the maximum is also observed at 800 °C, but the order is somewhat different: 800 °C > 500 °C > 1400 °C > 100 °C. There is a mismatch between leached anions (i.e. SO_4^{2-}) and cations, when they are expressed in equivalents (Table 2). This circumstance can be due to either the presence of other ions, such as Cl^-, together with those analysed, or to an analytical error, particularly in the gravimetric determination of sulphate. Interestingly, in terms of equivalents, the concentrations of leached SO_4^{2-} anions are lower compared with those of cationic species at the two lower heat-treatment temperatures, while a contrary situation is observed for the other temperatures. These differences can be understood since, as referred before, alumina and aluminium hydroxide particles develop a strong positive surface charge in aqueous media at ≈pH 4, attracting the ions of opposite sign charge (counter-ions), which might be specifically adsorbed.[14] Under these circumstances, they become more difficult to remove by leaching than co-ions. On the other hand, cationic species derived from salts, such as Al^{3+}, might be oxidised at higher temperatures forming much less soluble compounds.

The above results show that the washing process is clearly inefficient in the case of dried sludge. Efficiency in terms of either the elution rate or the total amounts removed increases with temperature increasing. However, temperatures higher than 800 °C are not recommended due to decomposition of aluminium sulphate, probably the most abundant sulphate in the sludge, added as flocculating agent.

Fig. 4 shows typical XRD spectra of the precipitates from the acidified supernatant solutions, confirming that they consist of pure $BaSO_4$ (JCPDS card 24–1035). All the peaks observed belong to $BaSO_4$. This is therefore an efficient way to remove the harmful sulphate species from the sludge and precipitating them as a practically insoluble salt,[19] which does not put any disposal or environmental problems.

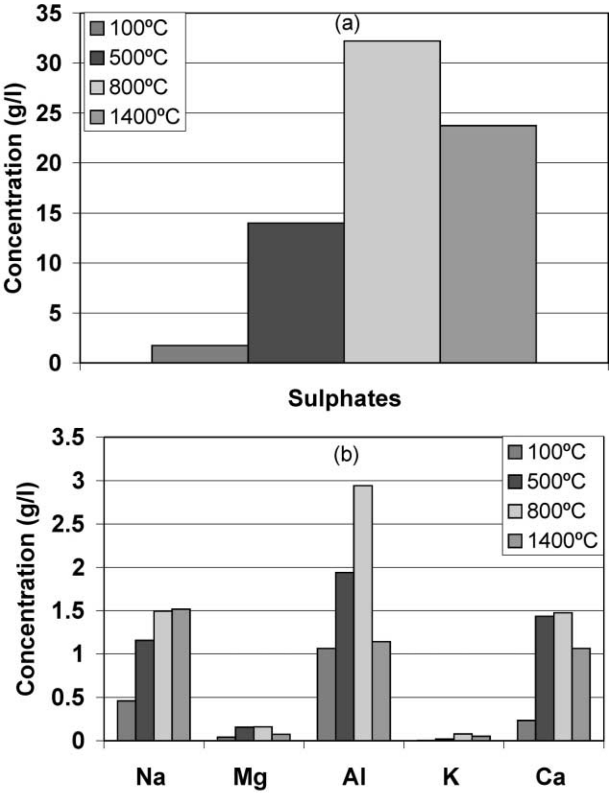

Fig. 3. Cumulative amounts of soluble species in the supernatant solutions after the washing procedure for the dried and calcined (at different temperatures) sludges: (a) sulphate; (b) cations.

Table 2
Equivalents of anions (i.e. SO_4^{2-}) and cations leached during washing the sludge calcined at different temperatures

Temperature of heat treatment (°C)	Leached species (eq.)	
	SO_4^{2-}	Cations
100	0.04	0.16
500	0.29	0.35
800	0.67	0.48
1400	0.49	0.25

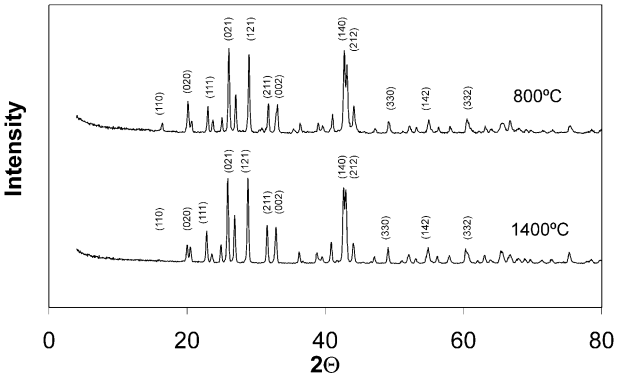

Fig. 4. XRD patterns of $BaSO_4$ obtained by precipitation from the supernatant solutions after the washing procedure for the sludge calcined at 800 and 1400 °C.

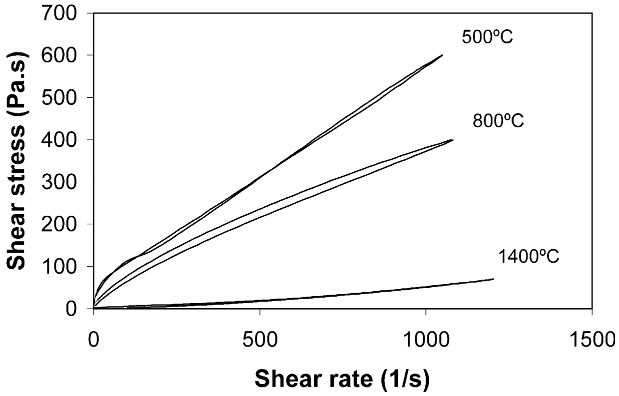

Fig. 5. Flow behaviour of the suspensions containing 30 vol.% solids from the sludge calcinated at 500, 800 and 1400 °C.

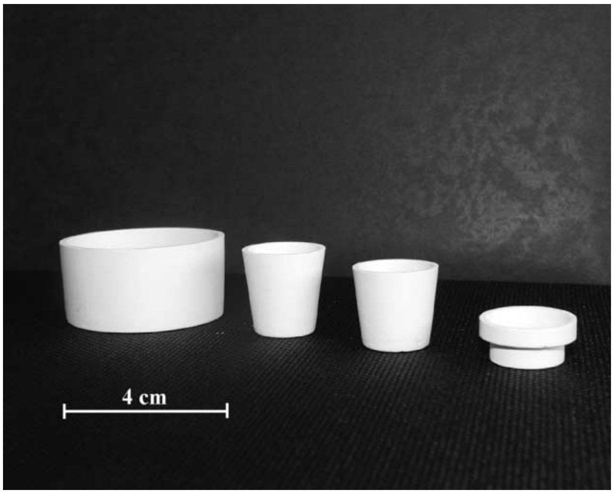

Fig. 6. Slip cast bodies obtained from the suspension containing 30 vol.% of the sludge calcined at 800 °C, after firing at 1600 °C for 2 h.

3.2. Influence of sludge treatments on powders' dispersing ability

It could be observed that during deagglomeration in a planetary mill at pH 4, the fluidity of the suspensions decreased with decreasing calcination temperatures. This is obviously related with the higher amounts of soluble species remaining in the powders, which could be slowly leached off along the deagglomeration process. The increasing difficulties encountered in reducing the size of agglomerates of powders calcined at lower temperatures may also account for the poorer flow properties. Therefore, the comparison of the rheological behaviour of suspensions prepared from different powders was carried out at 30 vol.% solids in the presence of a suitable amount of dispersant. Fig. 5 shows the flow curves of slurries derived from calcined sludges. It can be seen that the shear stress values at a given shear rate decrease significantly as the calcination temperature increases. The most significant differences are observed between 800 and 1400 °C. These results are according to the elution rates and the cumulative amounts of soluble species presented in Figs. 2 and 3, respectively.

The slip casting performance of different 30 vol.% tested slurries and of 20 vol.% slurry prepared from the dried and washed sludge was evaluated by pouring them into plaster moulds with a plaster/water ratio of 1.25:1. Green bodies from the 20 vol.% slurry (dried and washed sludge) exhibited poorly defined internal walls, high shrinkage values even before demoulding, and cracks, probably due to some density and humidity gradients. Contrarily, acceptable or good products could be consolidated from the 30 vol.% solids loading suspensions prepared from the sludges calcined at 500 °C or from those heat-treated at 800 and 1400 °C, respectively. Fig. 6 shows some almost full dense (0% water absorption) alumina crucibles obtained from the suspension containing the 800 °C calcined sludge and sintered at 1600 °C for 2 h. The linear shrinkage values were about 2.7% on drying, and 21.3% on firing. This last value is still relatively high compared with those usually experienced by ceramic products produced from commercial alumina powders. The difference may relay on the relatively low green density ($\approx$1.52 g cm^{-3}) of slip cast bodies. Attempts to improve it by using most suitable dispersion conditions are now underway.

4. Conclusions

The results presented and discussed along this work show that treatments involving calcination temperatures up to 800 °C followed by successive washings to remove the soluble species, can be a good method to be adopted towards recycling of Al-rich sludges to produce high-alumina refractory ceramics. The removal of soluble salts from the as-received sludges by washing is ineffective due to its gel-like consistency. Although the dispersing ability and the size of agglomerates decrease with increasing calcination temperatures, heat treatments at temperatures higher than 800 °C are not recommended due to the decomposition of aluminium sulphate and the release of harmful gaseous species to the atmosphere. The sulphate species could be efficiently removed by precipitation as $BaSO_4$. The washed powders could be used to fabricate alumina-rich ceramic products.

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References

1. Gonzales, E., Ansejo, J. L., Baena, A., Dufour, J., La Inglesis, A., Hernández, A., Cornejo, N., Ruiz-Ayúcar, E., Garcia, E., Ayala, N., Garcia-Carcedo, F., Delmas F. and Mayral, J. R. Application of anodising muds in several industrial fields. In: *Proceedings of Global Symposium on Recycling, Waste Treatment and Clean Technology—Rewas'99*, Vol. 1 (San Sebastián, Spain, September 1999), ed. I. Gaballah, J. Hager and R. Solozabal. TMS and INASMET, pp. 481–490.
2. Seabra, A. M., Pereira, D. A., Boia C. M. and Labrincha, J. A. Pre-treatment needs for the recycling of Al-rich anodising sludge as a ceramic raw material. In Proceedings of 1st Latin American Clay Conference, Vol. 2 (Funchal, Portugal, September 2000), ed. C. S. Gomes. Portuguese Clay Society, pp. 176–181.
3. Pereira, D. A., Couto, D. M. and Labrincha, J. A., Incorporation of alumina rich residues in refractory bricks. *CFI—Ceramic Forum International*, 2000, **77**(7), 21–25.
4. Dondi, M., Marsigli, M. and Fabbri, B., Recycling of industrial and urban wastes in brick production—a review. *Tile & Brick In.*, 1997, **13**(3), 218.
5. Pelino, M., Karamonov, A., Cantalini, C., Pisciella P. and Ulu, F. Glass–ceramic materials obtained from zinc-hydrometallurgy wastes. In: *Proceedings of Global Symposium on Recycling, Waste Treatment and Clean Technology—REWAS'99*, Vol. 1 (San Sebastián, Spain, September 1999), ed. I. Gaballah, J. Hager and R. Solozabal. TMS and INASMET, pp. 443–451.
6. Pereira, D. A., Aguiar, J. B., Castro, F. P., Almeida, M. F. and Labrincha, J. A., Mechanical behaviour of Portland of cement mortars with incorporation of Al-rich salt slags. *Cement and Concrete Research*, 2000, **30**(7), 1131–1138.
7. Perez, J. A., Terradas, R., Manent, M. R., Seijas, M. and Martinez, S. Inertization of industrial wastes in ceramic materials. Industrial Ceramics, 1996, **16**(1), 7–10.
8. Almeida, M. I. A., Amaral, M.R., Sousa Correia, A. M. and Almeida, M. F., Ceramic building materials: an alternative in disposal of sewage sludge. *Key Engineering materials*, 1997, **132–136**, 2280–2283.
9. Beretka, J., The utilisation of industrial wastes and by-products in the ceramic industry. *Journal of Australian Ceramic Society*, 1975, **11**(2), 25–29.
10. Tulyaganov, D. V., Olhero, S. M., Ribeiro, M. J., Labrincha, J. A. and Ferreira, J. M. F. Mullite-alumina refractory ceramics obtained from mixtures of natural common materials and recycled Al-rich anodising sludge. *J. Am. Cer. Soc.* Submitted for publication.
11. Ribeiro, M. J., Tulyaganov, D. U., Ferreira J. M. F. and Labrincha, J. A. Recycling of Al-rich industrial sludge in different ceramics bodies. *Ceramics International.* Submitted for publication.
12. Couto, D. M. S., Silva, R. F., Castro F. and Labrincha, J. A. Inertization of matallurgical sludges in clay-based ceramics. In: *Proceedings of 2nd Mediterranean Clay Meeting*, Vol. 2 (Aveiro, Portugal, September 1998), ed. C. S. Gomes. Portuguese Clay Society, pp. 214–219.
13. Parks, G. A., The isoelectric points of solid oxides, solid hydroxides, and aqueous hydroxo complex systems. *Chem. Rev.*, 1965, **65**, 177–198.
14. Tarì, G., Ferreira, J. M. F., Fonseca, A. T. and Lyckfeldt, O., Influence of particle size distribution on colloidal processing of alumina. *J. Eur. Ceram. Soc.*, 1998, **18**(3), 249–253.
15. Jeffery, G. H., Basset, J., Mendham, J. and Denney, R. C. In: *Vogel-Análise quimica quantitativa*, ed. Guanabara Koogan, S. A. Rio de Janeiro, Brasil, 1992.
16. Derjaguin, B. V., Landau, L. D., *Acta Physico-Chem.*, *URRS*, 1941, 633–662.
17. Verwey, E. J. W. and Overbeek, J. T. G., *Theory of the stability of lyophobic colloids*. Elsevier, Amsterdam, 1948.
18. Carcedo, F. *Recovery of Industrial Waste from Surface Treatment of Aluminium*. CENIM, Proyecto 783/D, Madrid, Maio, 1995.
19. Perry, R. H. and Chilton, C. H., *Chemical Engineers' Handbook*, fifth edn. McGraw-Hill, New York, 1973.
20. Carcedo, F. *Reutilización y minimización de residuos procedentes de la industria del aluminio de la comunidad de Madrid*. Proyecto: 07M/0080/1998, Madrid, 2001.