

Inertization of galvanic sludges by its incorporation in ceramic products

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Sludges produced by the physico-chemical treatments of waste waters generated by electroplating plants were physically and chemically characterised and incorporated in ceramic pastes. The influence of the amount of sludges added to a typical brick composition on the various processing steps and on the green and fired properties was studied. The environmental risks of the incorporation of these sludges rich in heavy metals such as Cr, Pb, Zn, Cu, Ni, etc. were evaluated by performing leaching tests on the fired products. The results showed that sludge contents up to 15 % could be incorporated without affecting significantly the physical characteristics of the ceramic products. Furthermore, a successful inertization of the pollutants was achieved.

Key words: Recycling, Sludges, Heavy metals, Environment, Wastes.

Inertización de lodos galvánicos para su incorporación a productos cerámicos

Se han caracterizado desde el punto de vista químico y físico lodos procedentes de las aguas residuales de procesos de galvanizado. Posteriormente se han incorporado a pastas cerámicas, convencionales de la industria ladrillera, estudiándose la influencia de las cantidades añadidas sobre las propiedades de los materiales tanto en verde como en el producto final y durante las distintas etapas de fabricación. Se evaluaron los riesgos medioambientales derivados de la incorporación de los metales pesados, tales como Cr, Pb, Zn, Cu, Ni etc, presentes en los lodos, mediante la realización de ensayos de lixiviado. Los resultados indican que puede incorporarse hasta un 15% en peso de dichos lodos, sin que se produzcan cambios significativos en las propiedades físicas de los materiales cerámicos obtenidos. Se ha obtenido, asimismo, un procedimiento viable de inertización de los agentes contaminantes.

Palabras clave: Reciclado, lodos, metales pesados, medioambiente, residuos

INTRODUCTION

Industrial activities produce a large variety of solid wastes and residues containing hazardous inorganic compounds that are usually accumulated elsewhere (1). Some of them are accumulating at an alarming rate and there is increasing public concern regarding the environment and ecology (2-3). Sludges produced by the physico-chemical treatment of waste waters generated by electroplating plants contain appreciable amounts of mobile heavy metals and are considered as potential eco-toxic residues (4). Hydrometallurgical treatment methods have been proposed to solve this problem, but the high compositional heterogeneity of these sludges from different treatment plants makes this objective a very difficult task to achieve.

Clay minerals usually exhibit good cation exchange capability, due to their surface charge properties, and could be used to trap harmful heavy metals ions. For instance, adsorption / desorption of cations on mineral surfaces, interlayer substitutions, mineral weathering reactions and clay catalysis are in some aspects closely related to the surface charge characteristics of the minerals involved (5-7). However, the fixation of these metal ions by cation exchange does not eliminate the possibility of leaching. On the other hand, clay minerals have typical mineralogical compositions involving silicate phases, which can dissolve considerable amounts of metals in the structure. Furthermore,

the possibility to form solid solutions is enhanced at high temperature. Therefore, the incorporation of residues containing ions of heavy metals such as Cr, Pb, Zn, Cu, Ni, etc., into a ceramic matrix can be a promising way to inertize them and avoid environmental risks.

Over the last decades many works have been written about the reuse, in the brick industry, of a wide range of urban and industrial wastes (2-3, 8-9). However, the number of studies aiming the recycling and inertisation of the sludges coming from electroplating industries are scarce (10). The aim of the present work is to incorporate sludges produced by the physico-chemical treatment of waste waters generated by electroplating plants into clay-based ceramic products and evaluate the effects of the amount added on mechanical strength, firing shrinkage, water absorption and leaching behaviour of the sintered materials.

2. EXPERIMENTAL

2.1. Physico-chemical treatment of industrial waste waters

Waste water derived from metallic surface treatments with Cr, Ni, Zn, Cu, etc. having relatively high concentrations of

heavy metal ions and cyanides were treated through a number of chemical reactions and physical separation of solid and liquid phases such as, oxidation of cyanides, reduction of Cr(VI), homogenisation and neutralisation, flocculation, decanting and filter-pressing. The cakes of metal-hydroxide sludges obtained contain usually about 35 wt% water and considerable amounts of greasy matter that have been already used to protect metallic surfaces from oxidation. Due to defects, which can be produced by organic components, the sludges were calcined at 900°C for 2 h followed by ball milling for 6 h. Chemical composition of the calcined sludges was determined by ICP spectrometry.

2.2. Formulation of ceramic pastes and preparation of testing samples and characterisation techniques

A plastic red clay containing α -quartz, illite, montmorillonite and a small amount of kaolinite, and a low-grade clay containing mainly α -quartz, and small amounts of dolomite, albite, muscovite and kaolinite (Campos S. A., Portugal) were used in the present work. In a first set of experiments, the two raw materials were wet mixed in three different proportions (50/50, 40/60, and 30/70 - pastes P1, P2 and P3, respectively). Cylindrical testing samples with a diameter of 10 mm and a length of 150 mm were prepared by vacuum extrusion, carefully dried at room temperature for 2 days, followed by complete drying at 110°C for 24h. The unfired dry cohesion was then evaluated by breaking at least 16 test pieces using an electromechanical universal testing machine Shimadzu 25AG, (Japan) at a load rate of 0.06 MPa.s⁻¹. The mechanical resistance was then calculated according to the ASTM C 689-93 Standard.

The testing pieces were fired at different temperatures (950, 1000, and 1050°C) using a heating rate of 120°C/h and hold for 2 h at the maximum temperature. Then, the mechanical

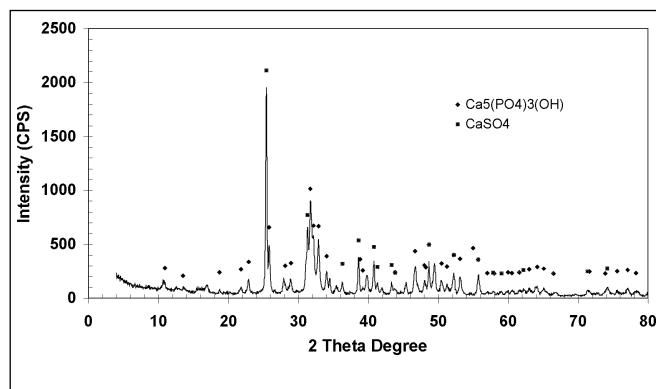


Figure 1. XRD pattern of the sludges calcined at 900°C.

resistance, firing shrinkage and water absorption were measured. Based on the results obtained, the intermediate composition, P2, was chosen as a reference for comparing with the other compositions containing sludges. In a second set of experiments in order to test if there is any practical limitation regarding their incorporation into ceramic products, different proportions (5, 10 and 15 wt% - pastes P4, P5 and P6, respectively) of the reference paste (P2) were replaced by the same amount of calcined sludges. The pastes obtained were characterised in the same way as described above. Chemical compositions of the as received and calcined sludges were determined by using an X-Ray Fluorescence Analysis instrument (PW 14000 Philips, Holand).

3. RESULTS AND DISCUSSION

Results of chemical X-Ray Fluorescence Analysis of uncalcined and calcined sludges are reported in Table I. It can be seen

TABLE I.
CHEMICAL X-RAY FLUORESCENCE ANALYSIS OF THE SLUDGES AS RECEIVED AND AFTER CALCINATION AT 900°C, 2H.

Major constituents (%)			Minor constituents (ppm)		
Oxides	Uncalcined	Calcined	Elements	Uncalcined	Calcined
MgO	< 200 ppm	0.04	Zr	9	12
Al ₂ O ₃	0.31	0.31	Sr	90	94
SiO ₂	0.27	< 200 ppm	Rb	23	23
CaO	46.63	54.44	Pb	73	77
TiO ₂	0.04	0.04	Ba	51	38
Fe ₂ O ₃	0.74	0.88	Sn	7	8
MnO	0.02	0.03	Zn	6448	6540
Na ₂ O	0.22	0.20	Cu	25	27
K ₂ O	0.07	0.08	Ni	1287	1316
P ₂ O ₅	27.31	31.05	Cr	702	699
S	7.31	11.32	V	25	31
L.O.I.	15.91	0.92			

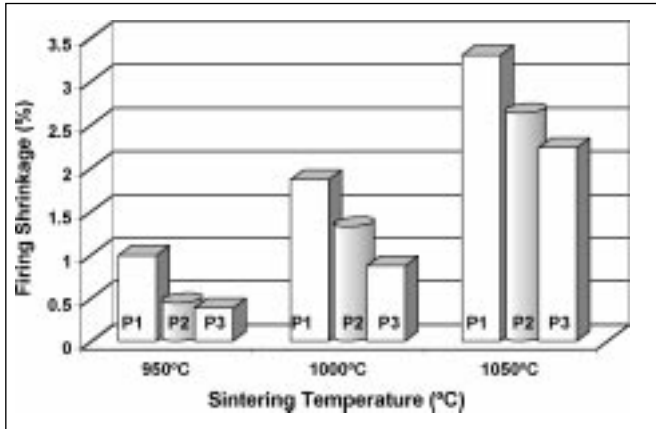


Figure 2. Evolution of firing shrinkage with the proportion between plastic and non-plastic clay components and temperature.

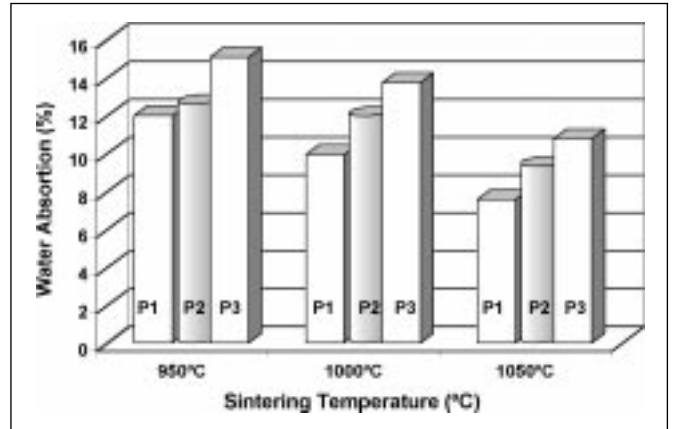


Figure 3. Influence of temperature and the proportion between plastic and non-plastic clay components on water absorption.

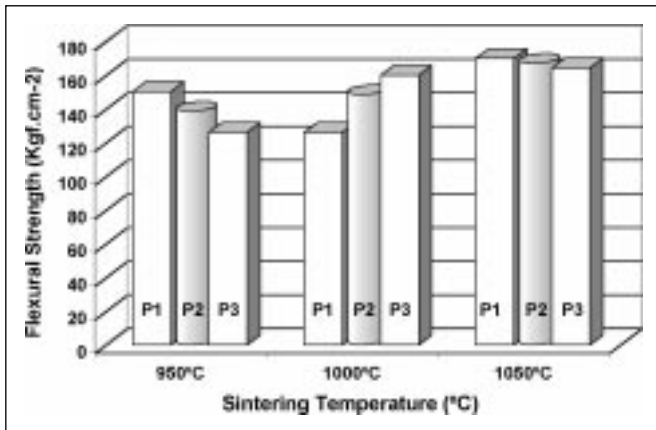


Figure 4. Influence of temperature and the proportion between plastic and non-plastic clay components on flexural resistance.

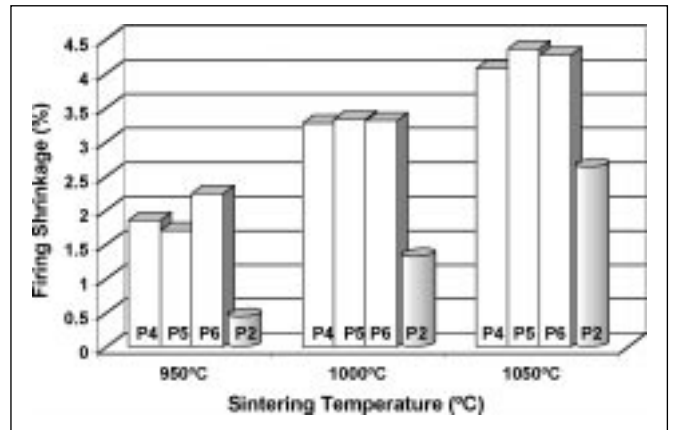


Figure 5. Effect of the amount of sludges added and temperature on firing shrinkage.

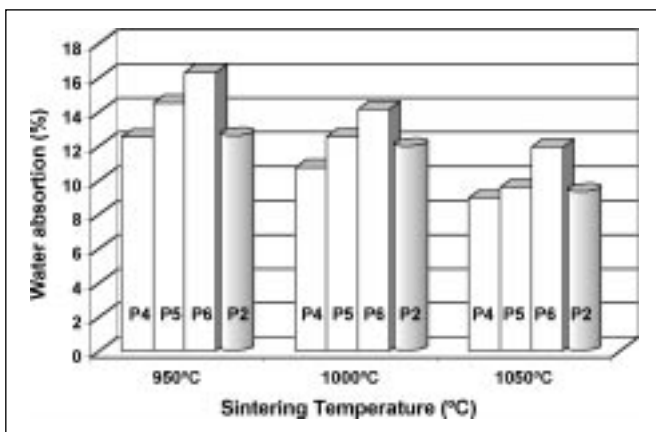


Figure 6. Effect of the amount of sludges added and temperature on water absorption.

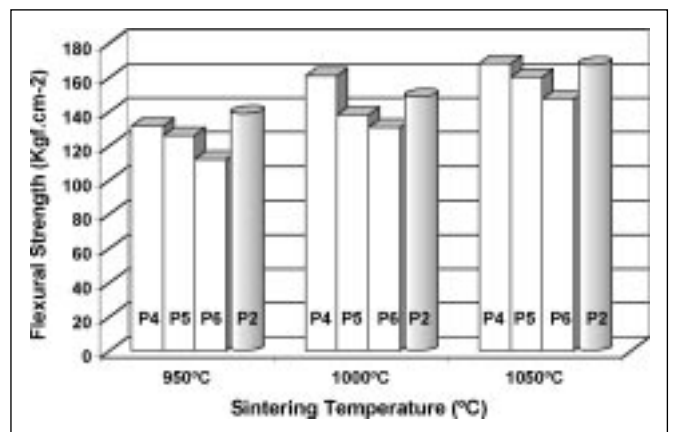


Figure 7. Effect of the amount of sludges added and temperature on flexural resistance.

that the composition is complex, including several oxides, being the main constituents CaO and P_2O_5 . During sintering, these components can react with each other and with the other constituents of the paste and form new crystalline phases. This explains why calcium sulfate (anhydrite, JCPDS Card Number 37-1496) and hydroxylapatite (JCPDS Card Number 9-432) were the only crystalline phases identified by XRD in the sludges calcined at 900°C (Figure 1). The uncalcined sludges experimented a weight loss of about 16%, even after complete drying at 110°C. This can be attributed to decomposition of metal hydroxides and to the burn-out of the greasy matter. Table I also shows appreciable concentrations of the elements Zn, Ni, Cr, Sr, and Pb. Traces (< 5 ppm) of other elements (Th, W, Nb, Y, Co) not reported in Table I were also detected.

It is known that the mechanical resistance of unfired ceramic products is improved by enriching the composition with the plastic component. However, the sensitivity to drying and total shrinkage also increase with increasing amounts of plastic clays and a good compromise between these requirements has to be established. The paste P2 exhibited good extrusion properties and closely matches and industrial brick composition.

The technological properties of sintered pastes without sludges are shown in Figures 2 to 4, while those of the compositions containing sludges are reported in Figures 5 to 7. For the first set of Figures, it can be observed that the firing shrinkage increases with increasing firing temperatures, and is always higher for the composition P1, while the water absorption shows an inverse trend. The flexural strength tends to be also higher for the composition P1 at the lower temperature and reaches similar values at the higher temperature. The evolution observed at the intermediate temperature was not expected and may derive from any experimental error. Other hypothesis is that mineralogical/chemical composition of different pastes and production of intermediate amorphous phases affect the flexural strength at 1000°C.

As stated above, the paste P2 exhibited good extrusion properties and its composition closely matches and industrial brick composition. Accordingly, the fired properties of the paste P2 are very similar to those exhibited by the products fabricated from that industrial brick composition and justifies the selection of P2 as the reference paste.

Figure 5 shows that the firing shrinkage of the pastes containing sludges are more or less independent of composition; only a slightly increasing trend with the amount of sludges added is suggested. Like in the previous case, firing shrinkage

also increases with increasing firing temperature, being always higher than that of the reference paste. However, water absorption increases with increasing amounts of sludges added. The results presented in Figures 5 and 6 lead to the conclusion that sludges enhance the pore volume fraction of the ceramic products. This might be due the chemical nature of the residues and/or to its aggregated state promoted by the calcination treatment that was not completely destroyed by milling. As a consequence of the increasing porosity with increasing amounts of sludge, the flexural strength tends to decrease. However, the mechanical strength of the composition with 5 wt% sludge is comparable with that of the reference paste at all temperatures tested. The technological properties of these pastes compare favourably also with values reported in the literature (11-12) for the same type of ceramic products. No significant colour differences were observed between the reference paste and the compositions containing sludge.

For one brick factory that processes about 300 t/day of raw materials, an incorporation ration of about 0.1% will be more than enough for consuming the whole amount of sludges produced by one treatment plant. Such a low amount of residues added does not affect the technological properties of the ceramic products. If the incorporation of higher amounts is desired, the possibility of moisture expansion to occur in long term applications should be considered.

Static leaching tests by distilled water were performed on pastes P2, P4, P5 and P6 fired at 1000°C, following the procedure established into the German standard methods for examination of water, waste water and sludge, DIN 38 414. The samples used in flexural strength tests were broken down in small pieces and 100 g of this material was put into 1000 ml of distilled water for 24 h. Then, the liquid phase was separated by filtration and chemical analysis was performed by ICP spectrometry (Table II). It can be seen that the amounts of toxic elements removed are clearly under the legal limits and that there is no significant difference between the reference paste and the other compositions containing sludge. This is a good indication that the incorporation of this type of residues into ceramic products is an efficient inertization method.

4. CONCLUSIONS

The results presented in this work enable us to conclude that the incorporation of toxic sludge from electroplating industry into a traditional ceramic matrix is a good inertiza-

TABLE II.
CHEMICAL ANALYSIS (ICP SPECTROMETRY) OF THE LEACHING TESTS.

Composition	Elemental concentration (mg/l)						
	Cr	Zn	Pb	Ni	Fe	Cu	Al
P2	0.010	< 0.010	< 0.025	< 0.010	< 0.010	< 0.010	< 0.015
P4	0.010	0.011	< 0.025	< 0.010	< 0.010	< 0.010	< 0.015
P5	0.015	< 0.100	< 0.025	< 0.010	< 0.010	< 0.010	< 0.030
P6	0.040	< 0.100	< 0.025	< 0.01	< 0.010	< 0.010	< 0.015

tion method even for incorporation rates much higher than those at which sludges are produced.

The firing shrinkage tends to increase with increasing amounts of added sludges. However, the other technological properties, including the colour of the fired red-clay products are practically unaffected by the incorporation of the residues.

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