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Physical and chemical characterisation of metal finishing industrial wastes

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Abstract

In EU countries approximately 150,000 tons/year of galvanic sludges are generated by 4000 industrial units from the corresponding wastewater treatment plants. These sludges are generally classified as hazardous (European Waste Catalogue as adopted in Council Decision 2000/532/CE and as amended by Decisions 2001/118/EC, 2001/119/EC and 2001/573/CE), basically due to the presence of heavy metals. This work attempts to better understand the physical and chemical characteristics of these sludges, by studying 39 samples collected in different Portuguese industries that should represent all kinds of similar wastes independent of their place of generation. Chemical composition and leaching characteristics are given, together with density, grain size distribution, and specific surface area values. Statistical analysis was used for grouping the wastes according to chemical parameters, which might be useful to predict potential reuse as raw materials for different applications.

Keywords: Galvanic sludge; Chemical composition; Leaching behaviour; Classification

1. Introduction

Metal plating requires a combination of several deposition and finishing operations. Chromium and zinc-plating, passivation, phosphatising and metal colouring operations are generally used to obtain a good substrate for further painting and deposition of organic agents in order to provide corrosion protection and decoration. For example, anodising is an electrolytic process that converts the metal surface into an insoluble oxide coating, which confers corrosion protection and might assure special electrical and mechanical properties (Lawrence, 1996; Kushner and Kushner, 1994).

Liquid effluents from those processes are generated by the mixture of washing waters and the saturated baths that are substituted regularly. In general, their treatment involves a precipitation process using hydroxides that might involve several steps: (i) Cr reduction (from the hexavalent to trivalent state) in acidic conditions (pH between 2 and 3, controlled by the addition of HCl or H_2SO_4) by adding iron chloride ($FeCl_2$), sodium sulphide (Na_2S), or (more commonly, since kinetics are the highest) sodium bissulphite ($NaHSO_3$); (ii) pH neutralisation (pH near to 8.5) by adding $Ca(OH)_2$, NaOH or a mixture of both; (iii) coagulation and flocculation. The suspension that results from the flocculation is then filter-pressed to partially remove the water. Typical solids content is under 40% (Magalhães, 2002), which imposes strong constraints on the transport and manipulation of the material. Apart from the water and some soluble salts, the sludge is composed of metallic species and processing additives. Its composition is mainly related to processing conditions and the following types might be encountered (Castro, 1999):

(i) Cr-plating for brass decoration, neutralised by the use of caustic soda;
(ii) Cr-plating for brass decoration, neutralised by the use of lime;
(iii) Ni-plating;
(iv) Zn-plating without cyaniding;
(v) Cu-plating;
(vi) mixed or multiple plating (Cr, Ni, Cu, Zn, Au, Ag, Cd, etc.);
(vii) Al-anodising or surface treatment;
(viii) phosphatising.

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These sludges are often classified as risky or hazardous wastes by environmental agencies (e.g. European Union Commission Decision 2001/573/EC). According to the European Waste Catalogue as adopted in Council Decision 2000/532/CE and as amended by Decisions 2001/118/EC, 2001/119/EC and 2001/573/CE, these wastes belong to the family CER 19 02, including those wastes generated by specific physico-chemical operations (e.g. Cr-deplating, decyaniding, neutralisation). Based on current estimates, about 4000 and 150,000 tons/year are generated in Portugal and EC countries, respectively (Castro, 1999; Kushner and Kushner, 1994). The dangerous character and toxicity is related to the high concentration of leachable species, such as heavy and/or transition metals, such as Cr and Ni. According to Viguri et al. (2000), the removal of those species depends on their ultimate equilibrium form and, particularly, on the pH values of the surrounding environment. Here, toxicity characteristics are assessed from leaching tests. Leaching tests in distilled water (DIN 38414-S4) indicate that the leaching levels of Ni and Cr are not directly predictable by the solubility of corresponding hydroxides, since the mobility is mainly related to the composition of the residue. As previously mentioned, sludge composition is determined by actual processing conditions which can change depending on operation conditions. Because the processes are discontinuous, the composition of the sludge can vary with time and between the baths. Therefore, the sampling plan must be long enough and rigorous to identify these variations and the respective causes, as suggested by many authors (Perez et al., 1996; Alleman, 1987; Komissarov et al., 1994; González et al., 1999; Almeida et al., 1997; Martelon et al., 2000).

This work attempts to better understand the physical and chemical characteristics of these sludges, by studying 39 samples collected in different Portuguese industries that should represent all kinds of similar wastes independent of their place of generation. Chemical composition and leaching characteristics are given, together with density, grain size distribution, and specific surface area values. Statistical analysis was used for grouping the wastes according to chemical parameters, which might be useful to predict suitability for reuse and inertization matrixes/processes, such as ceramization (Magalhães et al., 2004a,b).

2. Experimental

For this study, around 40 Portuguese metal-plating industries were visited and inquiries were made about the amount and nature of the generated sludges in order to get a representative picture of this important sector. Different processing conditions and locations were carefully selected, with some dominance of the North region (Braga and Aveiro districts, Table 1). Sample sorting and collection methodology depended on the availability of internal disposal conditions: (i) reasonably mixed sets from well equipped units; (ii) less well-homogenized samples, requiring the use of lab-scale mixing procedures to get homogeneous representative samples.

Table 1
Production type and location of sludges collected in this survey

Reference	District	Amount (tons/year)	Generating process
An	Aveiro	21	Al-anodising
Ad	Lisboa	550	Al-anodising
Al	Santarém	80	Al-anodising
Bb	Viseu	50	Non-cyaniding Zn-plating
Cc	Aveiro	10	Cr-plating for decoration
Cz	Aveiro	0.2	Polishing resines
Dt	Braga	4	Cr-plating for decoration
Ex	Braga	4	Cr-plating for decoration
Fr	Lisboa	250	Non-cyaniding Zn-plating
Fs	Porto	4	Cr-plating for decoration
Fx I	Braga	50	Cyaniding Zn-plating
Fx II	Braga	6	Phosphatising
Fq	Braga	7	Non-cyaniding Zn-plating (20%)
Jd	Braga	20	Cr-plating for decoration
Jl	Braga	15	Cr-plating for decoration
Lc	Braga	5	Al-anodising
Lm	Braga	3	Cr-plating for decoration
Mc	Aveiro	3	Multiple (mixed)
Mr	Porto	20	Al-anodising
Mn	Braga	12	Non-cyaniding Zn-plating & others
Mt I	Braga	10	Galvanising bath sludge
Mt II	Braga	30	Pickling
Ml	Braga	8	Cr-plating for decoration
Mg	Aveiro	4	Non-cyaniding Zn-plating
Mb	Aveiro	1	Multiple (mixed)
Mo	Braga	3	Cr-plating for decoration
Pc	Aveiro	100	Non-cyaniding Zn-plating
Pi	Porto	3	Cr-plating for decoration
Pm	Braga	12	Zn and Ni-plating
Rg	Braga	10	Zn, Cu and Cr-plating
Sf	Braga	2	Cr-plating for decoration
Sh	Braga	2	Cr-plating for decoration. The sludge was obtained after evaporation
St	Porto	2	Cr-plating for decoration
Sx	Lisboa	1	Multiple (mixed)
Tm	Braga	90	Al-anodising
Tg I	Aveiro	10	Galvanising bath sludge
Tg II	Aveiro	10	Pickling
Uf	Viseu	500	Polishing resines
Vm	Lisboa	145	Al-anodising

Samples were air dried at room temperature (<40 °C) to constant mass before being divided and screened. The water content of the samples used for leaching was determined on a parallel sample by drying at 110 °C overnight. Moisture content (H) was determined in a special balance (Adam Co., model AMB 310). Particle size distribution of dried powders was obtained by a laser technique (Beckman Coulter LS 230) by previous dispersion in water.

The specific area (SSA) of dried samples was determined by the BET method (Gemini II 2370). The chemical composition of dried samples was determined by X-ray fluorescence (XRF, X Unique II Philips). Each sample (about 1 g) was then submitted to acid digestion and quantitative analysis (Al, Ca, Cu, Cr, Fe, Ni and Zn) of the corresponding eluate was done using atomic absorption spectrometry (AAS, GBC 904 AA). Mineralogical composition of previously calcined (at 1000 °C) samples was determined by X-ray diffraction analysis (Rigaku Denk Co.). Leaching tests were performed according to DIN-38414-S4 protocol, to determine metals mobility under neutral conditions (using distilled water). The DIN 38414-S4 test is a non-controlled extraction method where the sample is shaken in demineralised water during the experimental time of 24 h. The liquid(water)/solid ratio was 10 L/kg. The pH value of the leached material stabilizes very quickly. The EN 12457/1-4 test includes four parts, differing from each other by different liquid/liquid ratios (L/S) and/or different grain sizes. The part 4 with L/S = 10 L/kg and a maximum grain size of 10 mm is consistent with the test DIN 38414-S4. In fact, the German test (DIN 38414) served as a basis for the European standard leaching method EN 12457, and is now included in that European standard as the 4th part.

Sludges were also divided based on their chemical composition (AAS), by using multivariate statistical analysis of the relevant concentrations of (seven) metals, their production process and origin. In this work, the multivariate statistics were carried out by principal component analysis in the ADE-4 program (Thioulouse et al., 1997). The multivariate nature of the waste composition data (seven columns and 39 individual rows) implies that a preliminary examination of the similarities among individual wastes may be required to group the data set. In the first step, the principal component analysis (PCA) was applied for this purpose. Later, classical multivariate analyses were used for synthesizing each waste cluster characteristic. Principal component analysis is a projection method that intends to find projections of maximal variability. It looks for linear combinations (principal components) of the data set that are uncorrelated and show high variance. In this way, a small number of principal components can explain a large variance. For example, the two first components can explain more than 70% of the total variance. These two components define the first factorial plane. It is common to use this plan to project the position of the original variables and the localization of the samples.

3. Results

3.1. Physical characterisation of wastes

Pasty and green coloured is the general look of the plating sludges, due to high moisture levels and dominance of Cr and Ni species. In turn, aluminium-based sludges generated from anodising processes are mostly grey or white. The use of $FeCl_2$ might give reddish tonalities, being much darker (brown or grey) after calcination.

Table 2
Main mineralogical phases (XRD) detected in the calcined samples

Reference	Phases
An	Al_2O_3, $CaSO_4$
Ad	$Al_{1.92}Cr_{0.08}O_3$, $CaSO_4$
Al	Al_2O_3
Bb	$CaSO_4$, $Ca_5(PO_4)_3F$
Cc	$CaSO_4$, CaO, $Ni_{0.75}Cu_{0.25}O$
Cz	SiO_2
Dt	$NiCr_2O_4$, NiO
Ex	$NiCr_2O_4$
Fr	$Ca_2Fe_{1.05}Al_{0.66}Mg_{0.13}Si_{0.13}O_5$, ZnO
Fs	Fe_3O_4, $NiCr_2O_4$, SnO_2
Fx I	Fe_2O_3, $ZnFe_2O_4$
Fx II	$FePO_4$
Fq	$CaFe_2O_4$
Jd	$CaSO_4$, CaO, $Cu_{1.02}ZnNi_{3.27}O_{5.29}$
Jl	Cu_2OSO_4, $6CuOCu_2O$, $NiCr_2O_4$
Lc	Al_2O_3, $CuFe_3O_2$, SiO_2
Lm	$Ni_{0.95}Cu_{0.05}O$, $NiCr_2O_4$
Mc	$Ca_8H_2(PO_4)_6$, $Cr_{1.3}Fe_{0.7}O_3$, $Ni_{0.6}Zn_{0.4}O$, $Zn_{0.5}Ni_{0.5}FeCrO_4$
Mr	Al_2O_3
Mn	$(Ni,Zn)Fe_2O_4$, Zn_2SiO_4, ZnO
Mt I	Fe_2O_3, $ZnFe_2O_4$
Mt II	$Zn_{0.5}Ni_{0.5}FeCrO_4$, Fe_2O_3
Ml	$NiCr_2O_4$, $ZnCr_2O_4$
Mg	$ZnFe_2O_4$
Mb	$Ca_5(PO_4)_3(OH)$
Mo	CuO, SiO_2
Pc	$(Zn_{0.35}Fe_{0.65})Fe_2O_4$, Fe_3O_4
Pi	$(Al_{0.95}Cr_{0.05})_2O_3$, $CaSO_4$, Cr_2O_3,
Pm	Fe_3O_4, $ZnCr_2O_4$, ZnO
Rg	Fe_2O_3, ZnO
Sf	$ZnCr_2O_4$
Sh	$MgFeAlO_4$, Na_2SO_4, $Na_6(SO_4)(CO_3,SO_4)$
St	$(Cu_{0.2}Ni_{0.8})O$, $CuNi_{0.5}Mn_{1.5}O_4$, Ni_2SiO_4
Sx	$(Al_{0.95}Cr_{0.05})_2O_3$, $CaSO_4$
Tm	$Al_{1.92}Cr_{0.08}O_3$, $CaSO_4$, Cu_2SO_4, $Ca_4Al_6O_{12}(SO_4)$
Tg I	Fe_2O_3, $ZnFe_2O_4$, ZnO
Tg II	$ZnFe_2O_4$
Uf	ZnO
Vm	Al_2O_3, $CaSO_4$

Table 2 shows the main mineralogical phases found in calcined (1000 °C) samples, the majority of them being mostly amorphous before firing. Alumina and other binary oxides or spinels (showing different compositional complexity degrees), and calcium sulphate, are the main common phases. Binary oxides and spinels result from the thermal decomposition of the hydroxides, with further reactions between active/fluxing species, such as Cu, Ni, etc. The detection of other possible sulphates (Ca or Na) is difficult due to their low relative volumetric amount (under 5%). In general the degree of crystallinity is not very high (the peaks are not very intense, see Fig. 1).

Table 3 gives the relevant physical characteristics of the sludges. As expected, almost all wastes have very high

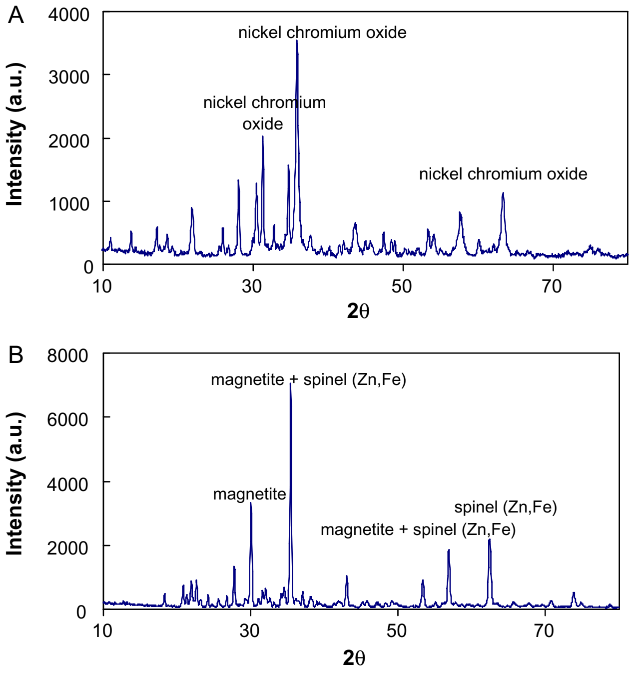

Fig. 1. XRD patterns of calcined sludges: (A) Sf; (B) Pc.

Table 3
Relevant physical characteristics of the sludges

Sludge	Moisture content (%)	90 vol% particles undersize (μm)	Powder density	SSA of dried sludge (m^2/g)	SSA of calcined sludge (m^2/g)
An	82.64	406	2.12	90.77	9.22
Ad	80.26	383	2.22	85.09	2.36
Al	79.85	410	2.17	92.44	1.42
Bb	45.6	117	2.51	27.74	0.01
Cc	44.72	120	2.50	14.09	1.91
Cz	5.99	34	1.55	32.87	8.45
Dt	87.85	63.2	2.24	32.19	1.49
Ex	70.94	286	2.67	38.88	9.18
Fr	74.76	428	2.61	43.81	2.38
Fs	49.55	376	2.49	82.86	16.51
Fx I	90.94	228	2.84	150.71	0.02
Fx II	23.31	58	1.47	158.17	0.07
Fq	70.8	526	2.65	48.88	1.42
Jd	60.9	206	2.49	41.29	0.93
Jl	74.89	262	2.47	54.06	3.15
Lc	60.5	32	1.98	29.62	4.98
Lm	80	265	2.68	12.43	3.67
Mc	53.77	337	2.40	51.72	1.38
Mr	80.47	480	2.21	153.51	53.06
Mn	70.73	263	2.29	65.71	0.22
Mt I	33.99	3	2.44	1.32	0.39
Mt II	42.48	4	3.32	68.86	2.25
Ml	79.48	268	2.54	18.68	7.81
Mg	71.11	452	2.53	39.01	0.01
Mb	53.22	389	1.72	50.27	2.83
Mo	69.93	448	2.62	81.66	1.54
Pc	68.11	280	2.58	73.94	0.06
Pi	83.19	407	2.27	49.81	29.23
Pm	75.92	415	2.69	87.61	0.10
Rg	2.3	438	2.82	79.27	0.21
Sf	89.31	288	2.73	23.84	4.62
Sh	35.09	122	2.44	7.40	0.97
St	89.88	213	2.52	11.95	0.92
Sx	75.16	24	2.39	43.88	0.17
Tm	77.74	397	2.22	106.53	0.98
Tg I	41.35	364	3.07	82.62	1.98
Tg II	36.42	5	3.14	85.67	0.56
Uf	59.83	330	2.00	0.71	0.22
Vm	79.11	400	2.14	73.82	1.74

SSA, specific surface area; calcination temperature = 1000 °C.

moisture levels (over 60 wt%). Powder density reflects the ratio between metallic and non-metallic components. Increasing this ratio seems to improve the density. The relationship with grain size distribution is not obvious, since results were obtained with non-dispersed samples. In this case, differences are very small since the determined size corresponds to agglomerates and not to individual grains. Most samples show maximum grain sizes of about 450 μm, confirming their fineness. Samples Mt, Tg II and Cz seem to be much finer as a consequence of consisting of dispersed particles, arising from pickling/polishing processes where metallic species are isolated. Moreover, the relative amount of non-metallic gels is much lower (tend to be denser), as predicted from the low moisture contents. This is also in accordance with relatively high dry density values and the dominating presence of oxides and spinels (XRD) on calcined samples.

SSA values of calcined powders reflect the dried starting conditions, in the sense that dried samples having higher SSA values are more reactive and sinterable. Upon firing and after decomposition is completed, particles tend to agglomerate and coalesce and final SSA values tend to decrease when compared to those of less reactive samples. However, a clear relationship between SSA and metals contents in sludges is difficult to establish. Only the elements Cu, Al and Cr appear to have some effect on SSA value, Eq. (1) giving the multiple regression inherent expression:

$$\mathrm{SSA} = -0.43\mathrm{Cu} + 0.10\mathrm{Al} + 0.38\mathrm{Cr} \tag{1}$$

For this multiple regression, the square of the correlation coefficient is only 0.55, despite the high significance level of the individual parameters (0.05% for Cu and Al and 0.001% for Cr). Fig. 2 shows the scatter plot for the linear regression between SSA and Cr content of the sludges. The negative effect of copper on SSA values is opposite to those of Al and Cr. The corresponding oxides of these last species are much less reactive/fluxing (highly refractory) and the sinterability is not promoted to the same extent (Norton, 1968). The effect of other reactive species (Fe, Ni, Zn), similar to that of Cu, is not significant to the behaviour of the sludge.

3.2. Multivariate analysis and clustering

Tables 4–8 give a division of samples based on their chemical composition (AAS). This division was achieved by using multivariate statistical analysis based on the

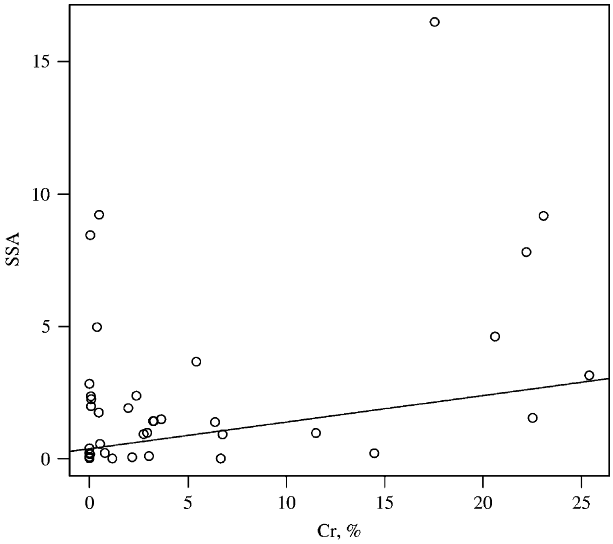

Fig. 2. Diagnostic plot for the linear regression between SSA and Cr content of the sludges.

relevant concentrations of metals, production process and origin (Fig. 3). Fig. 3 represents the best factorial plane formed by the first two factorial axes ($F1$, $F2$), which are the most stable axes derived from principal compound analysis (PCA) and accounting for 60% of the total sample variance: (A) represents the correlation circle, or the coordinates of the independent variables (metals concentration) in the factorial plan; (B) is the projection onto the first factorial plane created by PCA analysis of metals concentrations; and (C) gives the data which make possible the definition of the number of categories based on the nature of the producer.

The Shapiro–Wilks test was used to determine the distribution of the data (log-normal, normal or neither log-normal nor normal) at the 95% confidence level. The Shapiro–Wilks statistic (W) is the squared slope of the probability plot regression line compared to the sample sum of squares around the mean value. It ranges between 0 and 1. When data come from a normal distribution then the statistic is closer to 1. Thus, to test if data come from a normal distribution (with mean equal to the sample mean and deviation equal to the sample deviation) we compute the p-value as $\Pr < W$. If the p-value is below the pre-determined level of significance (0.05), then the null hypothesis is rejected. The null hypothesis tested by the Shapiro–Wilks test is observed when the data correspond to a normally distributed population. In general, this test is used for sample sets smaller than 50 units. If a larger number of samples is available then Shapiro–Francia or D'Agostino test is applied.

Five groups were obtained based on the PCA analysis and on the Shapiro–Wilks test.

Group I. Table 4 shows plating sludges belonging to this group that were processed by the use of $FeCl_2$. They are characterised by the highest amount of iron ($[\mathrm{Fe}] = 39.3\%$) and also by a high concentration of zinc ($[\mathrm{Zn}] = 11.7\%$). Concentrations of Ca, Cu, Cr and Ni show a non-normal dispersion.

Group II. Table 5 lists sludges that come from Zn-plating processes, easily distinguished by the highest amount of zinc ($[\mathrm{Zn}] = 28.4\%$). Fe and Zn are secondary and also representative species. The concentration of remaining elements is highly variable and corresponding variation coefficients (CV) are over 1. The change in total metals concentration follows a normal distribution, the average value being equal to 42.41% (standard deviation of 17.13%). This estimation has a confidence degree of 95%.

Group III. These sludges are generated from Al-anodising processes, being located in the fourth quadrant of Fig. 3. Their composition is well defined by Al and Ca concentrations, in a clear contrast to the remaining groups. The variations in Cu and Zn concentrations are the only ones that follow a non-normal distribution (Table 6). The average content of aluminium is 35.4% with a standard deviation value of 5.02%. In comparison with the first two groups, the total concentration of metals is lower (37.40%).

Table 4
Chemical composition of galvanic sludges processed with iron chloride in the wastewater treatment unit (Group I)

Sludge	Metals content (%)							
	Al	Ca	Cu	Cr	Fe	Ni	Zn	Total
Fx I	0.12	0.28	0.71	NA	43.7	6.40	2.14	53.32
Fq	0.11	10.16	0.51	3.27	31.89	0.01	0.48	46.43
Mt I	0.01	0.04	NA	NA	33.01	NA	16.6	49.62
Mt II	0.83	1.00	0.01	0.09	58.22	0.05	7.10	67.30
Tg II	0.41	0.24	NA	0.53	29.83	NA	32.2	63.19
Mean	0.30	2.34	0.25	0.78	39.3	1.29	11.7	55.97
Standard deviation	0.33	4.38	0.34	1.41	11.8	2.85	13.1	8.93
CV	1.13	1.87	1.38	1.81	0.30	2.21	1.11	0.16
Normality test of Shapiro–Wilks								
W	0.86	0.62	0.77	0.67	0.84	0.56	0.88	0.92
p	0.213	<0.01	<0.05	<0.01	0.165	<0.001	0.329	0.543

W is the Shapiro–Wilks statistic and is given by the squared slope of the probability plot regression line compared to the sample sum of squares around the mean value. Value p gives the significance level for data to show a normal distribution.

Table 5
Chemical composition of zinc-plating sludges (Group II)

Sludge	Metals content (%)							
	Al	Ca	Cu	Cr	Fe	Ni	Zn	Total
Fr	1.59	6.56	0.08	2.38	6.34	NA	18.3	35.29
Mn	0.08	0.33	0.03	0.78	6.93	0.01	37.5	45.70
Mg	0.53	0.63	0.04	6.66	0.07	0.22	15.4	23.58
Pc	0.13	2.19	0.64	2.17	12.3	0.57	26.9	44.89
Pm	0.05	0.22	0.67	3.02	13.4	1.12	32.4	50.83
Rg	0.18	0.22	3.62	14.5	4.83	2.04	47.4	72.78
Tg I	0.16	0.13	NA	0.08	2.80	NA	20.6	23.82
Mean	0.39	1.47	0.73	4.22	6.66	0.57	28.4	42.41
Standard deviation	0.55	2.36	1.30	4.98	4.80	0.77	11.5	17.13
CV	1.42	1.60	1.80	1.18	0.72	1.36	0.41	0.40
Normality test of Shapiro–Wilks								
W	0.663	0.652	0.624	0.793	0.948	0.804	0.947	0.979
p	<0.01	<0.01	<0.05	<0.01	0.716	<0.05	0.710	0.97

W is the Shapiro–Wilks statistic and is given by the squared slope of the probability plot regression line compared to the sample sum of squares around the mean value. Value *p* gives the significance level for data to show a normal distribution

Group IV. Table 7 lists the sludges generated from mixed/multiple processing/plating operations. As a natural consequence, their composition is very heterogeneous and the concentration variations of all species are far from a normal distribution. The two non-galvanic sludges Cz and Uf were grouped in this set. The total concentration of metals is only 19.99% (standard deviation of 10.01%), with a confidence level higher than 95%.

Group V. This group involves sludges generated from Cr-plating for decoration purposes. In general, Ni-plating precedes the chromium deposition, to get a suitable surfacial coating and as consequence Ni contents are normally very high (Table 8). A sub-division into two groups may now be considered based on the relative concentration of the two main species (see also Fig. 3): (i) *subgroup Va* contains sludges having higher chromium contents ([Cr] = 22.76%) and nickel concentration around 12%, and are very similar to those referred to by the Metal Finishing Association (Lindstedt, 1991) ([Cr] = 22.1% and [Ni] = 13.0%) for similar materials. The main differences are noted with zinc ([Zn] = 42.0%) and copper ([Cu] = 14.1%), which are higher than the current values (see Table 8); (ii) *subgroup V.b* consists of sludges that are chromium-poorer ([Cr] = 5.28%), and nickel-richer ([Ni] = 36.03%). The variation in total metals concentration again follows a normal distribution. In particular Cr concentration varies only within very restricted limits.

Apparently, the groups with lower variation coefficients are geographically concentrated, and this is a sign of a certain regional technological practice. As an example, wastes of the subgroup Va have Cr contents that are very similar and are all generated in the Braga district. By contrast, those of the Group IV are much less constant in composition and the corresponding producing units are geographically dispersed.

Table 6
Chemical composition of Al-anodising sludges (Group III)

Sludge	Metals content (%)							
	Al	Ca	Cu	Cr	Fe	Ni	Zn	Total
An	40.2	1.07	NA	0.49	0.21	0.08	0.01	42.06
Ad	38.4	1.22	0.06	0.07	0.07	0.06	0.02	39.95
Al	29.5	0.01	NA	3.23	0.25	0.13	0.01	33.17
Mr	30.5	0.16	NA	0.87	0.18	0.01	0.02	31.72
Vm	38.5	0.99	NA	0.47	0.09	NA	0.01	40.09
Mean	35.4	0.690	0.012	1.026	0.160	0.056	0.014	37.398
Standard deviation	5.02	0.560	0.026	1.264	0.077	0.053	0.005	4.626
CV	0.14	0.81	2.23	1.23	0.48	0.95	0.39	0.12
Normality test of Shapiro–Wilks								
W	0.809	0.833	0.552	0.755	0.920	0.942	0.684	0.852
p	0.096	0.146	<0.001	<0.05	0.530	0.685	<0.01	0.202

W is the Shapiro–Wilks statistic and is given by the squared slope of the probability plot regression line compared to the sample sum of squares around the mean value. Value *p* gives the significance level for data to show a normal distribution.

Table 7
Chemical composition of sludges generated from mixed processes (Group IV)

Sludge	Metals content (%)							
	Al	Ca	Cu	Cr	Fe	Ni	Zn	Total
Bb	0.19	16.4	NA	1.16	2.25	0.28	2.14	22.41
Cc	0.11	18.6	0.01	1.97	0.42	1.36	0.22	22.68
Cz	0.12	0.49	0.01	0.04	1.25	0.03	0.01	1.95
Fs	0.79	0.83	0.04	17.5	1.50	0.21	0.06	20.97
Fx II	NA	0.02	NA	NA	1.76	NA	2.95	4.73
Jd	0.25	9.33	5.85	2.75	0.34	5.84	4.01	28.37
Lc	8.94	0.04	0.32	0.38	1.27	0.02	0.02	10.99
Mc	0.20	0.40	0.51	6.37	8.13	1.01	2.58	19.20
Mb	0.08	12.5	0.02	NA	3.62	NA	0.08	16.32
Pi	18.9	0.35	1.11	15.3	0.85	1.33	0.60	38.43
Sh	0.10	0.06	2.24	11.5	0.25	2.64	1.54	18.33
Sx	0.19	11.6	NA	0.03	0.91	0.01	0.21	12.97
Tm	15.4	8.69	NA	2.93	0.41	NA	0.25	27.66
Uf	0.76	0.40	3.59	NA	0.21	0.01	1.91	6.88
Mean	3.284	5.695	0.979	4.285	1.655	0.910	1.184	17.99
Standard deviation	6.342	6.882	1.761	6.074	2.085	1.623	1.328	10.01
CV	1.93	1.21	1.80	1.42	1.26	1.78	1.12	0.55
Normality test of Shapiro–Wilks								
W	0.577	0.785	0.645	0.738	0.674	0.635	0.836	0.979
p	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.05	0.970

W is the Shapiro–Wilks statistic and is given by the squared slope of the probability plot regression line compared to the sample sum of squares around the mean value. Value *p* gives the significance level for data to show a normal distribution.

3.3. Leaching tests

Table 9 shows the average chemical composition of eluates from the water leaching of sludges under normalised conditions (DIN-38414-S4). Signed values (in bold) correspond to potential toxicity. The concentration limits used to define the hazardous nature of the leachates are defined by the European Council Decision 2003/33/EC. They are given

Table 8
Chemical composition of Cr and Ni-plating sludges (Groups Va and Vb)

Sludge	Metals content (%)							
	Al	Ca	Cu	Cr	Fe	Ni	Zn	Total
Ex	0.11	1.12	2.59	23.1	0.40	10.6	1.91	39.75
Jl	0.14	0.80	4.24	25.4	0.46	6.86	2.42	40.32
Ml	4.37	0.05	3.42	22.2	0.59	9.14	0.29	40.06
Mo	0.28	0.29	15.8	22.5	1.85	11.8	8.13	60.66
Sf	0.06	0.11	5.75	20.6	1.83	22.4	3.01	53.77
Mean	0.99	0.47	6.35	22.76	1.03	12.16	3.15	46.91
Standard deviation	1.89	0.47	5.39	1.74	0.75	6.02	2.96	9.72
CV	1.90	0.98	0.84	0.07	0.73	0.49	0.94	0.21
Normality test of Shapiro–Wilks								
W	0.590	0.886	0.748	0.995	0.752	0.832	0.855	0.784
p	<0.001	0.336	<0.05	0.773	<0.05	0.145	0.211	0.059
Dt	0.18	0.05	1.99	3.65	0.90	41.0	1.57	49.36
Lm	0.94	0.10	1.51	5.42	0.17	40.9	1.01	50.05
St	0.08	0.09	8.24	6.75	0.22	26.2	4.21	45.76
Mean	0.40	0.08	3.91	5.27	0.43	36.03	2.26	48.39
Standard deviation	0.47	0.03	3.75	1.56	0.41	8.54	1.71	2.30
CV	1.17	0.33	0.96	0.29	0.95	0.24	0.76	0.04
Normality test of Shapiro–Wilks								
W	0.836	0.893	0.803	0.993	0.801	0.756	0.877	0.867
p	0.203	0.363	0.122	0.844	0.117	<0.05	0.314	0.287

W is the Shapiro–Wilks statistic and is given by the squared slope of the probability plot regression line compared to the sample sum of squares around the mean value. Value *p* gives the significance level for data to show a normal distribution.

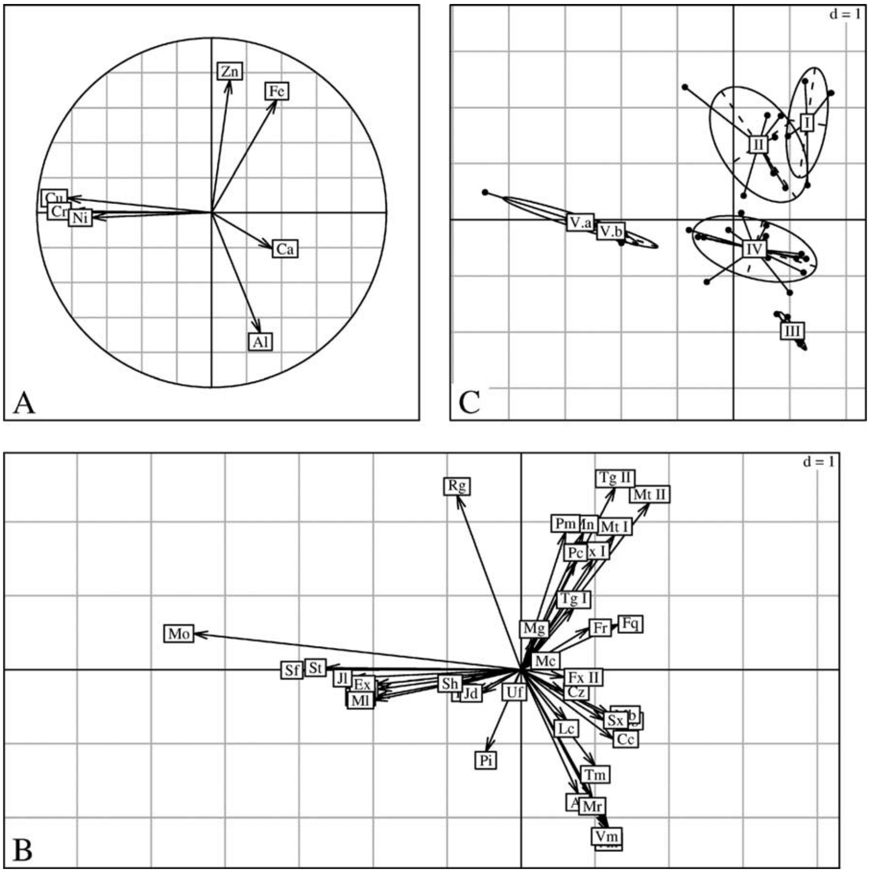

Fig. 3. Representation of the first factorial plane corresponding to 60% of the total variance: (A) correlations circle or either, the coordinates of the independent variables (metals concentrations) in the factorial plan; (B) sludges location onto the first factorial plane created by PCA analysis of metals concentrations; (C) relative location of the five groups defined according to the producer nature. ($d=1$ is the scale of the figure, corresponding to the squares side length used in the background grid).

in Table 10. Amongst the metallic species, nickel shows the highest leachability, but Cu and Zn are also easily leachable; on the contrary, aluminium shows the weakest solubility. Sulphate or chloride concentrations might also create problems in some cases. The leaching behaviour of the remaining elements is directly correlated with their concentration and is easily predictable from the group classifications given previously. As an example, sludges from Groups I, Va, and Vb show iron, chromium, and nickel, respectively, as maximum leaching species. Calcium and sulphates are easily removed from all samples, irrespective of their classification (chemical composition).

This work is very important not only as a tool for the quantification of generated amounts and characteristics of galvanic sludges, but (and more important) to predict suitable reuse and inertization matrixes/processes, such as ceramization (Magalhães et al., 2004a,b). Pre-treatment steps and adaptation of materials properties to a specific product can then be defined (Seabra et al., 2000). Highly reactive wastes upon firing might achieve strong immobilisation levels even in low temperature sintering products, like red-clay based ceramics (common building bricks and tiles). Sludges from Group I might behave in this way, since the overall metallic content is very high and iron is the most abundant specie. In this case colouring effects are predicted and their use in white products is restricted. Previous incorporation attempts (Couto et al., 2001) confirm these expectations, since the intrinsic fluxing character is beneficial in decreasing the firing temperature. At the same time, firing shrinkage is enhanced which requires special attention to prevent the appearance of warps and/or cracks (Pereira et al., 2000). Higher concentrations of mobile metals might also restrict the incorporation levels, due to potential toxicity of final products. Sludges belonging to Group III are expected to behave in a different way. Alumina will be the main phase after decomposition of dominant aluminium hydroxides, due to its well-known highly refractory characteristics. In this sense, the incorporation of this kind of waste will retard the maturation/sintering process of ceramic material and then decrease the physical and mechanical performance of products processed in unchanged conditions (Pereira and Labrincha, 2000; Tulyaganov et al., 2002). Low toxicity levels and slight colouring effects are the mainly expected advantages.

Table 9
Concentration of relevant species (mg/L) of eluates from the water leaching of sludges in normalised conditions (DIN-38414-S4)

Sludge	Al	Ca	Cu	Cr	Fe	Ni	Zn	SO_4^{2-}	Cl^-	pH
An	–	25.8	–	–	–	–	–	34.5	–	7.7
Ad	–	30.4	–	–	–	–	–	131	3.21	8.3
Al	–	2.43	–	–	–	0.24	–	44.9	8.67	8.0
Bb	–	302	–	–	–	–	0.15	162	2.71	7.3
Cc	–	121	–	–	–	–	–	66.7	9.47	8.2
Cz	–	47.5	–	–	–	–	–	6.7	93.5	7.6
Dt	–	1.24	–	–	–	**49.3**	–	94.2	–	7.4
Ex	–	16.3	–	0.43	–	0.96	–	63.6	–	7.1
Fr	–	44.2	–	–	–	–	0.71	35.2	21.1	7.5
Fs	–	–	–	–	0.16	0.25	–	42	92.7	10.4
Fx I	–	10	–	–	**57.6**	25.4	–	114	–	3.9
Fx II	–	9.91	–	–	–	3.3	–	17.7	33.5	3.6
Fq	–	60.6	–	–	–	–	–	1.7	487	7.7
Jd	–	121	–	0.57	–	–	–	136	–	8.9
Jl	–	15.8	–	0.73	–	0.81	–	180	2.8	7.5
Lc	3.54	2.47	**8.4**	–	1.25	**1.44**	**0.59**	12.3	9.78	2.8
Lm	–	8.2	–	–	–	**83.2**	–	123	539	7.7
Mc	–	5.11	–	0.35	–	–	–	6.8	–	8.8
Mr	–	–	–	–	–	–	–	27.5	–	8.2
Mn	–	2.69	–	–	–	–	0.49	10.6	7.59	8.5
Mt I	–	18.2	–	–	146	0.62	**5620**	–	**30,100**	3.8
Mt II	–	371	–	–	–	–	**5.86**	13.8	**1130**	6.4
Ml	–	7.76	1.06	–	0.06	**62.5**	–	130	115	4.1
Mg	–	4.33	–	–	–	–	0.48	5.2	9.52	7.8
Mb	–	44	–	–	–	–	–	0.5	44	7.8
Mo	–	2.24	–	17.8	–	0.35	–	34.8	–	8.2
Pc	–	82.9	–	–	–	–	1.07	5.4	231	7.7
Pi	–	12.2	–	–	–	2.6	0.14	79.3	42.3	6.3
Pm	–	1.94	1.31	–	–	–	–	6.3	19.2	8.5
Rg	–	19.3	1.41	–	–	**3.98**	–	128	468	6.8
Sf	–	1.33	–	12.3	–	–	–	69.6	6.78	7.3
Sh	–	0.66	**24.6**	**4580**	0.83	**10.1**	–	**837**	–	10.2
St	–	3.81	–	–	–	**80.5**	3.51	56.9	6.17	6.6
Sx	–	162	–	–	–	–	0.02	117	4.38	8.0
Tm	–	21.7	–	–	–	–	–	22.8	4.42	7.8
Tg I	–	2.36	**4.43**	1.37	1540	–	**318**	185	–	10.7
Tg II	–	2.52	–	–	–	–	0.12	123	273	8.7
Uf	–	83.4	–	–	–	–	0.02	0.2	0.38	11.2
Vm	–	29.8	–	–	–	–	–	77.5	0.66	7.8

Toxicity is denoted by bolded numbers.

Non-metallic components such as sulphates also require special technological attention, since their decomposition involves the escape of aggressive gases and might increase the number of pores.

4. Conclusions

A detailed picture of galvanic-type sludges was obtained in this survey, focused on Portuguese industries but easily replicated in other areas. The sludges were divided into five general categories, based mostly on the chemical composition, but assuming also leaching behaviour and some physical characteristics. These categories are: (i) plating sludges processed with $FeCl_2$; (ii) Zn-plating; (iii) Al-anodising; (iv) mixed/multiple processing/plating; (v) Cr-plating for decoration purposes. As expected, major leached species from each sludge correspond to its main components, but total leaching levels depend on the mobility of the species involved. Calcium removal was found to be relevant for almost all samples, irrespective of their nature since it is introduced in the wastewater treatment.

All the materials are made of fine particles or agglomerates and have very high moisture levels (above

Table 10
Concentration limits used to define the hazardous nature of the leachates, as defined by the European Council Decision 2003/33/EC

Specie	Concentration limit
Cr (VI)	0.1–0.5 mg/L
Cu	2–10 mg/L
Ni	0.4–2.0 mg/L
Zn	2–10 mg/L
Chloride	1.2–6.0 g/L
Sulphate	0.2–1.0 g/L

60 wt%). As-collected and dried samples were amorphous and basically made up of hydroxides and sulphates of the relevant metallic species. Thermal reactivity was also predicted based on SSA evolution and the type of phases formed upon sintering. All of these aspects are very helpful in predicting viable alternatives for reuse, for instance by incorporation in ceramic or cement-based materials. For example, Al and/or Cr-rich sludges are poorly reactive and their effective inertization in ceramic matrixes requires high sintering temperatures and/or effective mixing/milling operations.

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