ELSEVIER

Journal of Hazardous Materials A79 (2000) 63–75

Journal of Hazardous Materials

www.elsevier.nl/locate/jhazmat

Characterization of metal finishing sludges: influence of the pH

J. Viguri, A. Andrés, R. Ibañez, C. Ruiz Puente, A. Irabien *

Departamento de Química ETSII y T, Universidad de Cantabria, Avda. Los Castros, s/n. 39005 Santander, Spain

Received 26 November 1999; received in revised form 24 March 2000; accepted 26 April 2000

Abstract

Metal finishing sludges are classified as metal hydroxide hazardous wastes due to the heavy metal release to the environment. This release, commonly determined by compliance lixiviation tests based on the equilibrium conditions at the end of the leaching experiment, is mainly dependent on the pH of the solution. In this work, the leaching behaviour of Cd, Cr, Cu, Fe, Ni, Pb and Zn, of the 32 metal finishing sludges coming from 16 European industrial facilities, and using the distilled water compliance test DIN 38414-S4, have been studied. The concentrations of chromium and copper in the leachates do not follow the solubility evolution of their hydroxide with the pH. The simple assumption of a heavy metal concentration in the leachate directly related to the solubility of the hydroxide is not in good agreement with the experimental results of the distilled water leaching test, probably due to the presence of different species, which can contribute to the metal mobility depending on the sludge composition. An experimental evaluation of the easily available amount of metals in real wastes seems to be necessary for disposal assessment. This paper contains valuable information, from orderly handling metal finishing wastes to the statistical studies of production and management of wastes suggested recently by the Commission of the European Community.

Keywords: Metal finishing sludges; Characterization; Compliance test; pH leaching behaviour

1. Introduction

Waste management in metal finishing facilities can be divided into three general categories: process changes, maintenance of processes or facilities and on-site treatment.

* Corresponding author. Tel.: +34-42-201597; fax: +34-42-201591.
E-mail address: irabienj@ccaix3.unican.es (A. Irabien).

PII: S0304-3894(00)00248-X

The treatment of wastewater usually includes a physico-chemical facility, which generates sludge. The characteristics and metal amount of finishing sludges depend on the process, types of rinsing water and wastewater treatment. This sludge has been classified as a group of hazardous waste in the European Hazardous Waste Catalogue (EHWC) [1] with the code 19.02.01, described as metal hydroxide sludges, which suggests a waste behaviour related to metal hydroxides.

Recently, the Commission of the European Community has presented a Proposal of Regulation [2] establishing the framework to develop European statistics about waste production and management. In this proposal, the metal finishing sludges are classified in the 01.2 aggregation level as acid, basic and saline wastes. In order to establish environmental management options and assess their environmental impact, the metal finishing sludges require a previous characterization to distinguish between hazardous and nonhazardous wastes, despite the EHWC classification.

One of the main environmental impacts of metal finishing sludges is the leaching of pollutants to surface and ground water. Therefore, the leaching tests, which allow the determination of the leaching behaviour of pollutants, play a major role in assessing the classification, compatibility of use and treatment according to the environmental impact assessment of disposal or technical–economical possibilities of reuse within regulatory limits. In the European Economic Community Directive on the Landfill of Wastes [3], three levels of characterization are established: level 1 or basic characterization, where wastes should fulfill the defined criteria to be accepted in a reference list; level 2 or compliance test, where wastes should fulfill the opportune criteria at the entrance of the landfill; and level 3 or on-site verification of each load of wastes. Basic characterization procedures (level 1), compliance test (level 2) and on-site verification methods (level 3) do not yet have a common regulation in the European Union. Some regions and many landfill facilities in Spain [4–6] have adopted the DIN 38414-S4 compliance test with the limit values in the leachate chemical composition according to the 1991 EEC Landfill of Wastes Draft [7].

The batch-type leaching test, classified from a practical point of view as compliance test, is aimed at attaining equilibrium conditions at the end of the leaching experiment. In compliance test, several factors, such as extraction fluid, pH, major element chemistry, redox status of the systems and liquid-to-solid ratio, influence the release of contaminants from waste. The pH of the solution has been a critical parameter in determining the solubility of contaminants [8–10]. In fact, lower limits of heavy metal concentrations in the leachate are usually considered for distilled water compliance test and the higher limits are considered for acidic compliance test.

Published studies on industrial wastes show the leaching behaviour of heavy metal pollutants for an extensive list of inorganic waste materials as a function of pH. A general feature of the leaching test results obtained from coal fly-ash is a minimum metal leachability in the pH range from 7 to 10 [11]. Systematic trends have been found also in the leachability–pH relationship [11] of Municipal Solid Waste Incinerator (MSWI) ashes. Other studies with MSWI ashes [12,13] show a more complex leaching behaviour, depending on the pH and waste composition. The general trend in the leaching behaviour with pH from lead and zinc smelting slags has been found to be very similar for a given element, which is almost independent of the origin [14,15].

Predictions of the leaching behaviour of elements from pulverized coal fly-ashes could be derived on the leachate elemental concentration as a function of pH [14,16,17]. The leaching behaviour of Waelz-processed slags is largely solubility-controlled in the pH domain, ranging from pH 5 to 12, showing a release of heavy metals similar to slags with different basicity and levels of crystallisation [18]. Metal finishing sludges [9,19] have shown a V-shaped pattern of leached chromium with a minimum leaching concentration between pH 6 and 7, and a strongly enhanced leaching of copper, which has been explained by the concentration of soluble copper organic compounds.

Heavy metal solubility of metal finishing sludges has been assumed to be related to the solubility of their hydroxide, depending on the final pH of the leaching test [20]. Taking into account the complexity of industrial sludges and the low-regulatory metal thresholds in the compliance test, the metal concentrations in the leachates can be much higher than predicted, based on the solubilities of the hydroxides as a function of pH. Interactions in the liquid phase with soluble species showing effects, such as common ion, complex formation, changes in the ionic strength and/or redox potential, may lead to a leaching behaviour that cannot be easily related to the solubility of their respective hydroxides [12]. Differences in the leaching as a function of pH are generally caused by a limited number of chemical composition parameters, amount and kind of organics, soluble anions, sorption equilibria on iron hydroxides and reducing conditions [9–11].

In the present work, an experimental evaluation of 32 metal finishing sludges coming from 16 European facilities, using the compliance test without pH control DIN 38414-S4, has been performed. The leaching behaviour of Cd, Cr, Cu, Fe, Ni, Pb and Zn as a function of pH has been analysed and compared with the theoretical solubility of the corresponding metal hydroxides.

These results allow us to confirm that the application of characterization procedures of metal finishing sludges based on single batch-extraction test with distilled water and regulations of the metal concentration in the leachate must take into account the complex composition of these wastes, leading to a chromium and copper mobility, which is not related to the solubility of their hydroxide.

2. Materials and methods

2.1. Metal finishing wastes

Experimental work was performed on 32 sludges, collected in the form of filter cakes from the water treatment plant of 16 metal finishing facilities (G1–G16), with on-site treatment of wastewater, located in Cantabria and Basque Country regions (northern Spain) and Minho region (northwestern Portugal). The metal finishing facilities were selected because they are representatives of the metal finishing wastes produced at the studied regions [21]. The companies involved in this study include facilities whose primary business is the finishing of metal products coming from other firms or job shops, and facilities performing metal finishing as one of its production processes or captive shops. Both of them are classified in section D, subsections I, J, K, M and N into the NACE (statistical classification of economic activities) codes, which need to develop

Table 1
Limit concentrations of metals in the DIN 38414-S4 leachates [7]

Parameter	Hazardous waste range (mg l^{-1})	Inert waste
Lead	0.4–2.0	The total of these metals: < 5 mg/l[a]
Cadmium	0.1–0.5	
Chromium	0.1–0.5	
Copper	2–10	
Nickel	0.4–2.0	
Zinc	2–10	

[a]And no single value above the minimum fixed for hazardous waste.

statistical data about their metal finishing sludges [2]. The metal finishing processes include the common steps of cleaning and surface preparation by alkaline solutions of sodium hydroxide and acidic solutions of sulphuric and/or hydrochloric acid, followed by hard chromium plating (G1–G3), decorative chromium plating (G4 and G5), zinc plating and chromate-conversion coating (G6–G8), nickel and chromium electroplating (G9–G13) and anodizing of aluminium materials (G14–G16), leading to the five studied groups of wastes.

The sludges were generated after the physico-chemical treatment, where the metal finishing rinse wastewater, spent solutions and accidental discharges are treated. The treatment consists of successive steps of hexavalent chromium reduction, neutralization, flocculation, clarification and sludge dewatering. The obtained sludges are primarily inorganic wastes containing, as major pollutants, heavy metal hydroxides: Cd, Cr, Cu, Fe, Ni, Pb and Zn anions, depending on the metal finishing operation and minor amounts of organics. Further details of these wastes have been reported earlier [22].

2.2. Leaching behaviour of wastes

The compliance test used to study the metal leaching behaviour with pH is the leaching procedure DIN 38414-S4 [23], suggested as regulatory test for waste characterization before landfilling in the 1991 EEC Landfill Directive Draft [7]. This leaching test takes a liquid (deionized water)-to-solid ratio of 1 l/100 g, which is slowly stirred at 0.5 rpm for 24 h. The leachate is filtered and the pollutants are analysed. The components, which are determined in the DIN 38414-S4 leachates, are selected as a function of origin and qualitative composition of sludges. Analysis of metals (Cd, Cr, Cu, Fe, Ni, Pb and Zn) is performed using atomic absorption spectrometry, Perkin-Elmer, 1100 B. The experimental results are compared with the concentration levels proposed by the EEC Landfill Draft, which suggests the limit concentrations for the metals involved in this study, as shown in Table 1.

3. Results and discussion

Results of pH and metal concentration in leachates coming from the DIN 38414-S4 leaching procedure are shown in Table 2. The level of metal concentration and the kind

Table 2
Results of DIN 38414-S4 leaching of the metal finishing wastes

Waste sample	Chemical leachate composition (mg l^{-1})							
	Final pH	Cd	Cr	Cu	Fe	Ni	Pb	Zn
G1	8.2	0.10	0.53	0.06	0.29	0.24	0.11	0.04
G2-I	6.9	0.13	< 0.08	0.14	0.09	0.51	0.37	0.18
G2-II	7.3	0.05	< 0.08	0.10	0.13	0.20	0.50	0.16
G2-III	7.7	0.03	< 0.08	< 0.06	< 0.09	0.12	< 0.10	0.06
G3-I	9.1	0.08	3.76	1.26	0.20	0.67	0.35	0.11
G3-II	9.8	0.04	2.42	4.42	0.14	0.19	0.38	0.45
G4-I	7.7	0.06	n.d.[a]	< 0.06	< 0.09	0.36	< 0.10	n.d.
G4-II	7.7	< 0.02	< 0.08	< 0.06	< 0.09	0.26	< 0.10	0.06
G5-I	8.7	0.08	1.60	0.70	< 0.09	0.41	5.47	0.04
G5-II	8.5	0.05	1.12	< 0.06	< 0.09	0.20	0.27	0.07
G5-III	8.6	0.03	1.04	0.39	< 0.09	0.29	1	0.06
G6-I	7.6	0.02	0.08	< 0.06	< 0.09	0.40	< 0.10	0.02
G6-II	7.5	0.03	0.21	< 0.06	< 0.09	0.77	0.15	0.06
G7-I	7.5	< 0.02	< 0.08	< 0.06	< 0.09	< 0.10	< 0.10	70
G7-II	8.5	< 0.02	< 0.08	< 0.06	< 0.09	< 0.10	< 0.10	0.34
G8	9.0	< 0.02	6.40	< 0.06	n.d.	< 0.10	< 0.10	n.d.
G9-I	9.0	0.09	137	9.70	0.87	80	0.53	0.81
G9-II	8.7	0.07	234	3.31	0.22	68	0.23	0.18
G9-III	8.2	0.05	127	93	0.50	110	0.35	0.64
G10-I	6.2	0.05	< 0.08	0.06	0.29	< 0.10	0.27	23
G10-II	5.8	0.03	< 0.08	0.14	0.12	5.59	1.97	93
G11-I	12.4	0.04	< 0.08	0.19	0.13	0.48	0.51	0.69
G11-II	9.6	0.02	< 0.08	< 0.06	< 0.09	0.14	0.16	0.02
G12-I	8.3	< 0.02	1.99	0.21	< 0.09	5.40	n.d.	0.10
G12-II	7.9	0.02	34	5.70	< 0.09	13	0.11	2.17
G12-III	7.1	0.02	3	0.50	< 0.09	4.20	< 0.10	< 0.02
G13	6.5	< 0.02	< 0.08	0.30	n.d.	202	< 0.10	< 0.02
G14-I	9.7	0.03	< 0.08	< 0.06	< 0.09	0.10	0.15	0.02
G14-II	10.9	0.03	0.09	< 0.06	< 0.09	< 0.10	0.19	0.02
G14-III	10.4	0.02	< 0.08	< 0.06	< 0.09	< 0.10	0.21	0.02
G15	7.2	0.03	0.11	< 0.06	< 0.09	0.11	0.44	0.28
G16	7.5	< 0.02	0.51	< 0.06	n.d.	0.36	< 0.10	n.d.
Thresholds[b]	4–13	0.1–0.5	0.1–0.5	2–10	–	0.4–2	0.4–2	2–10

[a] n.d., Not determined.
[b] Standards for the landfill of wastes [7].

of metal present at each pH value is heterogeneous. An application of the concentration limits, suggested by the EEC Landfill Draft to the obtained results, shows that 22% of the samples should be classified as nonhazardous wastes and 78% of the samples should be classified as hazardous wastes. The chemical characterization of the leachates allows the identification of chromium as the main pollutant responsible for the classification of the wastes as hazardous, as shown in many cases by very high concentrations in the leachates.

Fig. 1 shows the behaviour of the different metal finishing sludges, based on the evaluation of the sum of the studied metals in the leachates as a function of pH. A high

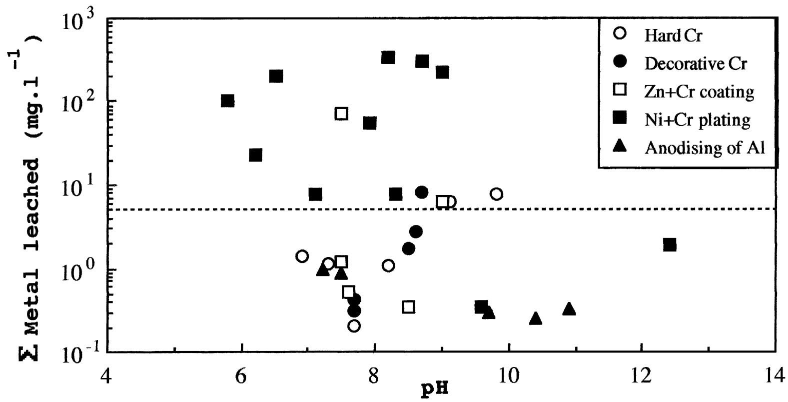

Fig. 1. Contribution of the metal finishing categories to the total metal leachability as a function of pH. Dotted horizontal lines are the concentration thresholds for total metal suggested by the 1991 EEC Landfill Draft [7].

dispersion of results does not allow the establishment of a clear general trend of the sum of metals in the leachate, according to the different metal species solubilities. The amount of metals in the leachate shows very different values, depending on the origin of the waste. Nickel and chromium electroplating wastes are leaching a sum of metals between 5 and 500 mg l^{-1}, which does not seem to be related to the pH; and anodising of aluminium wastes shows very low values of the sum of metals in all leachates.

Metal finishing sludges are complex mixtures of species, where the relationship between metal mobility and pH based on distilled water batch test may show the influence of some minor species of the metals in which solubility is not related to the pH. Leachates probably contain organic binders used as additives to metal finishing process solutions, such as solvents, wetting agents, catalyst, activators, chelating agents and organic acids. The heterogeneous results, which have been obtained for 32 real wastes coming from 16 different facilities, led to the conclusion that mobility of the metals in industrial wastes cannot be easily related to the pH influence in the solubility of the hydroxides, and that minor amounts of soluble metals species in the waste can be responsible for the dramatic changes in the concentrations of metals in the leachate.

The individual behaviour of cadmium, chromium, copper, iron, nickel, lead and zinc as a function of pH in the leaching of metal finishing sludges are shown in Figs. 2–8, where the solid lines in the figures describe the theoretical solubility curves for the hydroxides [24] and the dotted horizontal lines are the concentration thresholds suggested by the EEC Landfill Draft [7] for each metal.

Cadmium, iron and lead concentrations, as shown in (Figs. 2, 5 and 7), respectively, are always below the solubility of the hydroxides of the metals, and their behaviour with pH is near constant, which can be related to low quantities of cadmium, iron and lead in the wastes. The general behaviour with the pH of the zinc concentrations, Fig. 8, seems to be more consistent with the solubility of the metal hydroxide, although some values are above or below the solubility limits of their hydroxides.

Concentrations of chromium, copper and nickel, shown in (Figs. 3, 4 and 6), respectively, led to their evaluation as hazardous wastes, according to the thresholds

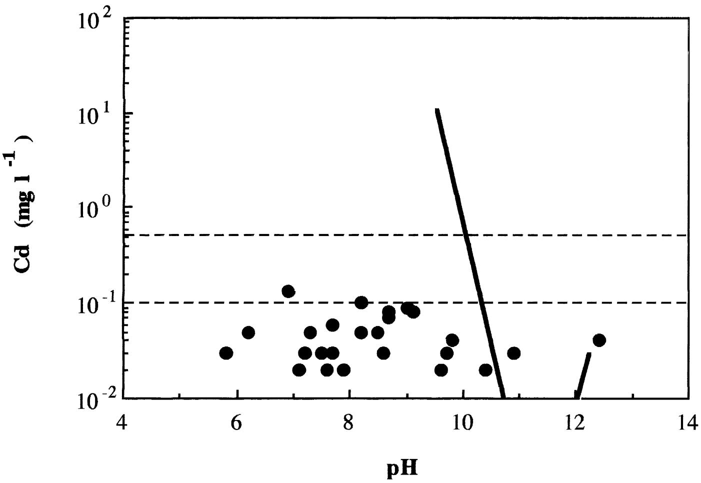

Fig. 2. Leachability of Cd from the metal finishing sludges as a function of pH. Dotted horizontal lines are the concentration thresholds for Cd suggested by the 1991 EEC Landfill Draft [7].

suggested for waste disposal given in Table 1, in the 1991 Proposal for a Council Directive on the Landfill of Wastes [7]. Wastes that eluate concentration within the range fixed for hazardous wastes should be treated before disposal and wastes that eluate concentration not above the maximum values fixed for inert wastes could be sent to inert waste landfill sites. The influence of pH on the concentrations of these metals in the leachates cannot be deduced from the solubility of the metal hydroxides. The solubility

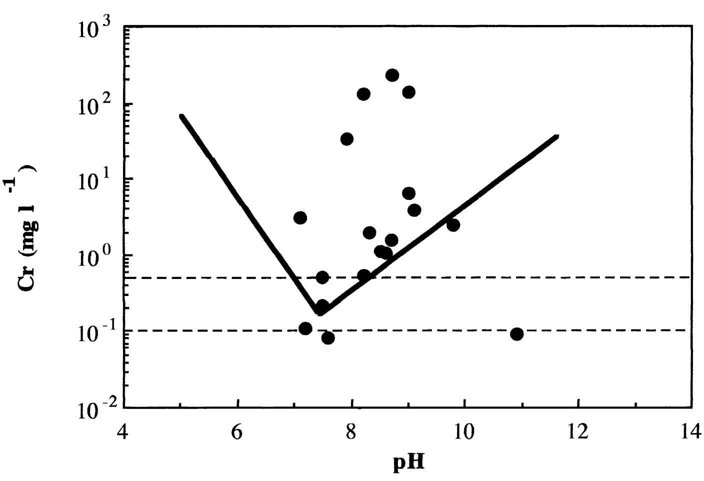

Fig. 3. Leachability of Cr from the metal finishing sludges as a function of pH. Dotted horizontal lines are the concentration thresholds for Cr suggested by the 1991 EEC Landfill Draft [7].

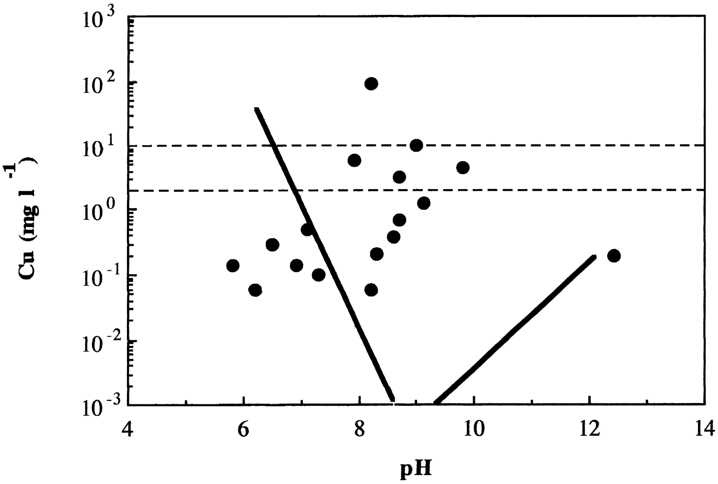

Fig. 4. Leachability of Cu from the metal finishing sludges as a function of pH. Dotted horizontal lines are the concentration thresholds for Cu suggested by the 1991 EEC Landfill Draft [7].

of chromium and copper is associated with the origin of the waste, as shown in Figs. 9 and 10, respectively.

An important number of experimental points showing concentrations of chromium that cannot be related to the hydroxide solubility as a function of pH are shown in Fig. 9 for nickel and chromium electroplating sludges. Soluble chromium species must be assumed in this waste in order to explain that pH values in the range between 7 and 9 are not able to fit the chromium concentration in the leachates below the limits of the suggested regulation of Table 1. Fig. 9 shows, by dotted lines, the fitting of the

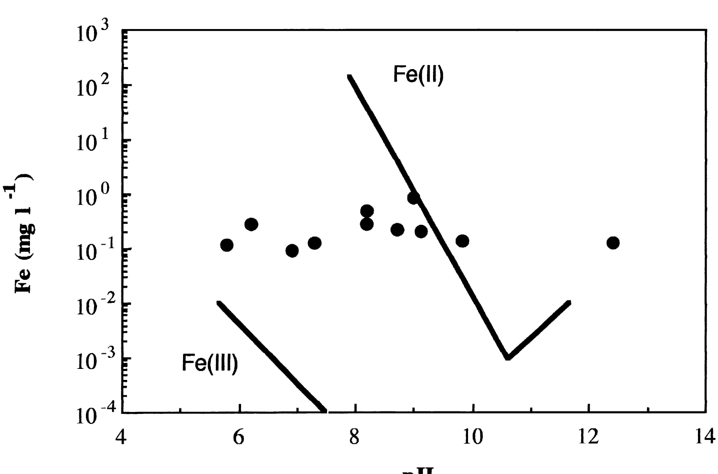

Fig. 5. Leachability of Fe from the metal finishing sludges as a function of pH.

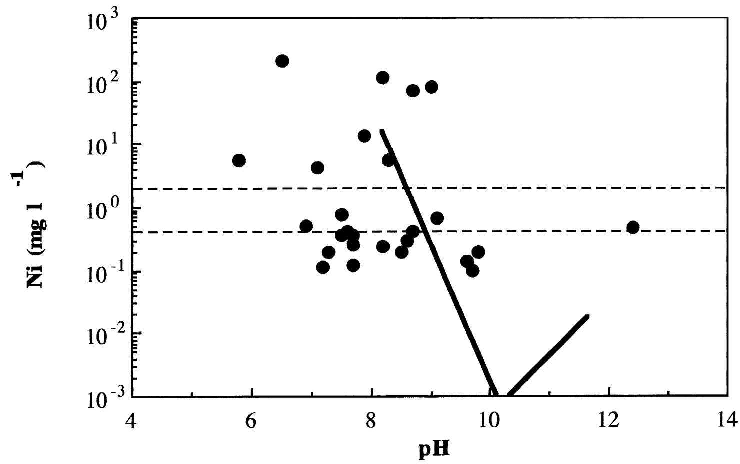

Fig. 6. Leachability of Ni from the metal finishing sludges as a function of pH. Dotted horizontal lines are the concentration thresholds for Ni suggested by the 1991 EEC Landfill Draft [7].

chromium behaviour with the pH obtained with the nickel- and chromium-plating wastes.

An enhanced solubility of copper, taking the solubility of copper hydroxide as reference, is shown in Fig. 10 for hard chromium, decorative chromium and nickel–chromium electroplating sludges. Because of this, soluble copper species should also be assumed in the leachate of these kinds of wastes. In the same way, Fig. 10 shows, by dotted lines, the behaviour of the pH obtained with the hard chromium-plating wastes, and nickel- and chromium-plating wastes.

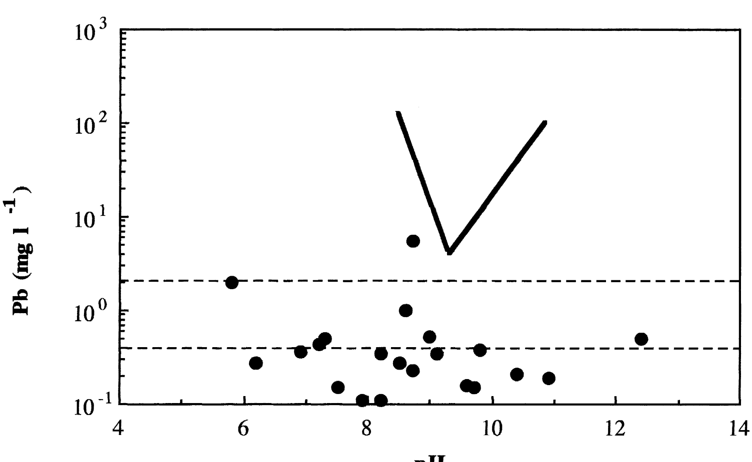

Fig. 7. Leachability of Pb from the metal finishing sludges as a function of pH.Dotted horizontal lines are the concentration thresholds for Pb suggested by the 1991 EEC Landfill Draft [7].

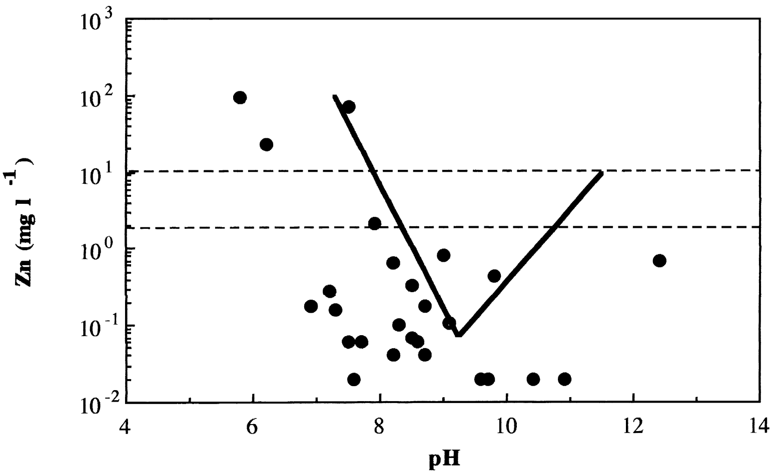

Fig. 8. Leachability of Zn from the metal finishing sludges as a function of pH. Dotted horizontal lines are the concentration thresholds for Zn suggested by the 1991 EEC Landfill Draft [7].

The concentration of chromium and copper in the leachates as functions of pH is very different to the concentrations, which can be expected from the solubility of the hydroxides, and it depends on the origin of the waste, although metal finishing sludges have been classified by a waste code 19.02.01, which takes as reference "metal hydroxides" [1]. This experimental evidence makes individual studies for each group of metal finishing wastes necessary, making the generalization of the metal-leaching

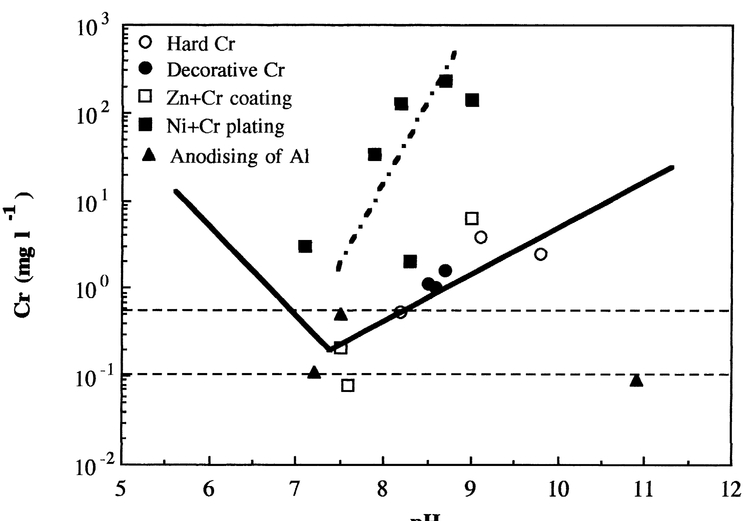

Fig. 9. Leachability of Cr from the different metal finishing activities as a function of pH. Dotted horizontal lines are the concentration thresholds for Cr suggested by the 1991 EEC Landfill Draft [7].

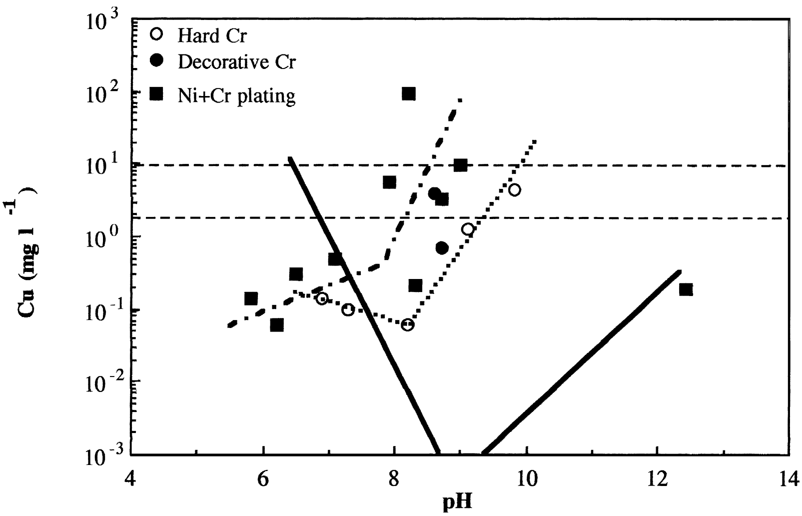

Fig. 10. Leachability of Cu from the different metal finishing activities as a function of pH. Dotted horizontal lines are the concentration thresholds for Cu suggested by the 1991 EEC Landfill Draft [7].

behaviour that could be applied to the characterization of metal finishing sludges difficult. The amount of soluble metal species, which may contain the real waste, shows a very important influence in the results of distilled water compliance tests.

Changes in the composition of the leachant (water), due to the solubility of anions, organics and metal impurities, have shown an important influence in the concentration of heavy metals, leading to strong deviations from the solubility of metal hydroxides. V-shaped curves, typical of the solubilities of metal hydroxide as a function of pH, are not in good agreement with the experimental findings of this paper, probably due to the amount of readily available species of metals in the wastes closely related to the generation process of waste.

4. Conclusions

The batch test DIN 38414-S4, based on distilled water leaching, has been applied to 32 metal finishing sludges coming from 16 on-site physico-chemical treatment plants of metal finishing wastewater, encoded by the same European Waste Code 19.02.01. Concentrations of chromium and copper in the leachates do not show the pH influence, which could be expected from the solubility of the hydroxides. The experimental mobility of metals as a function of pH is far from a systematic behaviour, which cannot be assumed in the characterization of metal finishing sludges for disposal.

This experimental behaviour shows the evidence that soluble chromium and copper species based on minor components of the metal finishing sludges are able to enhance the total amount of chromium and copper in the leachate, leading to unexpected high concentrations of the total amounts of metals, which are not related to the low solubilities of their hydroxides.

This work shows that readily available species of chromium and copper are present in the studied finishing sludges, which needs to be taken into account in the environmental management of such wastes. The mobility of hazardous metals in metal finishing sludges has been often neglected assuming ideal behaviour of metal hydroxides, which is not in good agreement with the experimental behaviour found in 32 different European wastes.

References

[1] European Economic Community (EEC), European Hazardous Waste Catalogue (EHWC). DOCE no. L 356, Brussels, 1994, p. 14.
[2] European Economic Community (EEC), Council project of Regulation on the management of wastes statistics. COM (99) 31 final-99/0010 (CNS) (1999/C87/02), Brussels, 1999, pp. 22–96.
[3] European Economic Community (EEC), Council Directive on the Landfill of Wastes. DOCE No. L 182, Brussels, 1999, p. 1.
[4] Ibañez R., Contribution to industrial wastes characterization. PhD thesis, University of Cantabria, Santander, Spain, 1996.
[5] A. Andrés, I. Ortiz, A. Irabien, Fresenius Environ. Bull. 1 (1992) 172.
[6] I. Ortiz, R. Ibañez, A. Andrés, A. Irabien, Fresenius Environ. Bull. 4 (1995) 189.
[7] European Economic Community (EEC), Proposal for a Council Directive on the Landfill of Wastes, Draft on 33 May 1991, COM (91), 102 final-SYN 335, European Economic Community, Brussels, 1991.
[8] Ph. Quevauviller, H.A. van der Sloot, A. Ure, H. Muntou, A. Gómez, G. Rauret, Sci. Total Environ. 178 (1996) 133.
[9] O. Hjelmar, H.A. van der Sloot, in: H.A. van der Sloot, L. Heasman, Ph. Quevauviller (Eds.), Harmonization of Leaching/Extraction Tests, Stud. Environ. Sci. vol. 70 Elsevier, Amsterdam, 1997, pp. 131–171.
[10] H.A. van der Sloot, Waste Manage. 16 (1996) 65.
[11] H.A. van der Sloot, in: J.J. Goumans, H.A. van der Sloot, Th.G. Aalbers (Eds.), WASCON 91: Waste Materials in Construction, Stud. Environ. Sci. vol. 48 Elsevier, Amsterdam, 1991, pp. 19–36.
[12] A.M. Fällman, B. Aurell, Sci. Total Environ. 178 (1996) 71.
[13] T. Eighmy, J. Eusden, K. Marsella, J. Hogan, D. Domingo, J. Krzanowski, D. Stämpfli, in: J.J. Goumans, H.A. van der Sloot, Th.G. Aalbers (Eds.), WASCON 94: Environmental Aspects on Construction with Waste Materials, Stud. Environ. Sci. vol. 60 Elsevier, Amsterdam, 1994, pp. 111–136.
[14] D.S. Kosson, H.A. van der Sloot, in: J.J. Goumans, G.J. Senden, H.A. van der Sloot (Eds.), WASCON 97: Waste Materials in Construction. Putting Theory into Practice, Stud. Environ. Sci. vol. 71 Elsevier, Amsterdam, 1997, pp. 201–215.
[15] D. Mandin, H.A. van der Sloot, C. Gervais, R. Barna, J. Mehu, in: J.J. Goumans, G.J. Senden, H.A. van der Sloot (Eds.), WASCON 97: Waste Materials in Construction. Putting Theory into Practice, Stud. Environ. Sci. vol. 71 Elsevier, Amsterdam, 1997, pp. 617–630.
[16] R. Garavaglia, P. Carasmucio, in: J.J. Goumans, H.A. van der Sloot, Th.G. Aalbers (Eds.), WASCON 94: Environmental Aspects on Construction with Waste Materials, Stud. Environ. Sci. vol. 60 Elsevier, Amsterdam, 1994, pp. 87–102.
[17] J. Fruchter, D. Rai, J. Zachara, Environ. Sci. Technol. 24 (1990) 1173.
[18] H.R. Bae, R. Barna, J. Mehu, H.A. van der Sloot, P. Muszkowick, C. Desnoyers, in: J.J. Goumans, G.J. Senden, H.A. van der Sloot (Eds.), WASCON 97: Waste Materials in Construction. Putting Theory into Practice, Stud. Environ. Sci. vol. 71 Elsevier, Amsterdam, 1997, pp. 647–660.
[19] P.A. Cnubben, H.A. van der Sloot, in: J.J. Goumans, G.J. Senden, H.A. van der Sloot (Eds.), WASCON 97: Waste Materials in Construction. Putting Theory into Practice, Stud. Environ. Sci. vol. 71 Elsevier, Amsterdam, 1997, pp. 247–251.
[20] J.R. Conner, Commercial fixation and solidification of hazardous wastes, Van Nostrand-Reinhold, New York, 1990.

[21] M.M. Monteiro, in: MOPU (Ed.), Residuos Tóxicos y Peligrosos. Tratamiento y Eliminación, Madrid, 1989, p. 449.
[22] J. Viguri, R. Ibañez, A. Andrés, I. Ortiz, A. Irabien, Environ. Technol. 20 (1999) 171.
[23] DIN 38414 S4, German standard procedure for water, wastewater and sediment testing. Group S (Sludge and Sediment). Determination of leachability (S4). Institüt für Normung. Berlin, 1984.
[24] US EPA. Federal Register. 52(155):29999, August 12, 1987.