

Study on the Immobilization of Cr (VI) and Cr (III) in Geopolymers Based on Coal Combustion Fly Ash

Yolanda Luna Galiano¹, Guray Salihoglu², Constantino Fernández Pereira¹, José Vale Parapar¹

¹University of Seville, School of Industrial Engineering, Department of Chemical and Environmental Engineering, Camino de los Descubrimientos s/n E-41092, Seville, Spain

²Uludag University, Faculty of Engineering and Architecture, Environmental Engineering Department, 16059, Bursa, Turkey

Abstract

The immobilization of chromium (III) and (VI) in geopolymeric matrices are studied in this paper. The geopolymers were prepared using coal combustion fly ash as the main aluminosilicate source. The influence of the activating solution has been studied using different solutions such as potassium silicate, sodium silicate, potassium hydroxide and sodium hydroxide. In addition, some samples containing Ordinary Portland Cement (OPC) and the same activating solutions were prepared for comparative purposes. Mixtures were cured at ambient temperatures and in an oven at 60 °C. After curing, samples were subjected to different leaching tests such as UNE-EN 12457-4 and USEPA TCLP tests to assess the efficiency of the immobilization of Cr in both oxidation states. The total chromium leached was generally less than 0.05 % of the total Cr (III) added, in spite of the fact that a partial oxidation of Cr (III) to Cr (VI) was observed in most Cr (III) samples. With regard to Cr (VI), the immobilization was more problematic. Thus, the total chromium leached was between 2.4 - 4.8% of the total Cr (VI) added, the immobilization achieved with potassium hydroxide being better than that achieved with sodium hydroxide. Moreover, the use of OPC alone as a binder showed better leaching results than coal fly ash. No significant differences were found regarding Cr immobilization between the two curing conditions used.

1. INTRODUCTION

Geopolymer technology has recently received attention in various applications. In one of them, geopolymers are being used as binders in waste stabilization/solidification (S/S) systems of heavy metals containing waste. In the immobilization of toxic metals geopolymer systems function similarly to cement binders in terms of encapsulation, however, they have improved chemical and physical properties, such as structural integrity, low permeability, high compressive strength and durability [1, 2]. Low permeability is the property that favors the use of these materials as immobilization systems for hazardous

metals [3]. The mechanisms of encapsulation are believed to be either physical or chemical where metals are taken into the geopolymer network and possibly bound into the structure for charge balancing roles or remain physically trapped by the surrounding network [4].

Some ash-based geopolymer systems have been used to improve the immobilization of metals such as Cu, Pb, Cs, Sr, As Cd and Cu, in S/S solids [2, 5, 6, 7, 8, 9, 10] with metals incorporated into the matrix. The results show that these heavy metals can be effectively immobilized into the geopolymeric matrices.

Cr is a heavy metal that can be found in many industrial wastes in two oxidation states, Cr (VI) and Cr (III). The trivalent form is relatively nonreactive and less toxic than the hexavalent form, which is very toxic and creates health problems for humans [11].

Some authors have studied chromium stabilization using alkali-activated matrices. Thus, Deja [12] studied the immobilization of Cr (VI) in an alkali-activated slag binder and showed that Cr (VI) incorporation led to a stronger binder. However, Palomo and Palacios [11] observed a complete failure of geopolymeric setting upon addition of 2.6 wt% Cr⁶⁺ as CrO₃. This latter observation was attributed to the formation of Na₂CrO₄·4H₂O, which then inhibited geopolymeric setting. However, another study [10] showed that the addition of chromium as Na₂CrO₄ actually gave an increased compressive strength at 28 days. The same paper above [11] showed that Cr (VI) immobilization is quite ineffective, although its addition as sparingly soluble salt is somewhat better than as soluble salt.

The present paper is therefore concerned with the stabilization of chromium in fly ash-based geopolymer binders in simulated waste containing Cr⁶⁺ and Cr³⁺ ions, and the effect of the composition of these geopolymers on the metal immobilization efficiency.

2. EXPERIMENTAL

2.1. Materials

Low calcium coal fly ash (ASTM class F) from the combustion of high quality pulverized coal in the biggest coal power plant in the south of Spain, Los Barrios (550 MW), was used as the main silicoaluminate agent. Ordinary Portland Cement (OPC, type II) was used for comparative purposes. The main elements of the S/S agents are detailed in Table 1. Potassium and sodium silicate solutions (KSil and NaSil, respectively) were used as activating solutions, and they were supplied by Industrias Químicas del Ebro (Zaragoza, Spain). The soluble silicate product specifications are listed in Table 2. Sodium and potassium hydroxide 8M were also used as activating solutions.

Table 1.
Main elements of Fly ash and OPC

	Moisture 105 °C	LOI 750 °C	Main Elements (% w/w)						
			Fe ₂ O ₃	CaO	MgO	SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O
FA	0.05	3.32	5.86	3.94	1.84	63.91	21.51	0.68	1.67
OPC	0.15	-	2.15	61.7	2.76	21.2	5	0.13	0.16

Table 2.
Specifications of sodium and potassium silicate solutions

	SiO ₂ , %	K ₂ O, % (Na ₂ O, %)*	SiO ₂ /K ₂ O (SiO ₂ /Na ₂ O)*	Density 25 °C, g·cm ⁻³
NaSil*	25.5-28.5	7.5-8.5	3.04-3.8	1.296-1.396
KSil	23.1	10.6	2.18	1.31

2.2. Preparation of S/S solids. Preparation of geopolymers

Different mixtures were prepared maintaining the fly ash and chromium contents constant and varying the activating solutions. The activating solution contents were adjusted to achieve the same workability in all the mixtures. With the mass obtained, cylindrical plastic moulds (30 mm diameter and 41 mm height) were filled and compacted. Finally, samples were vibrated for 5 minutes in order to release bubbles. During curing, some samples were placed in a stove at 60 °C while others were stored at room temperature. In addition, hydraulic binders such as OPC were used instead of fly ash and in combination with fly ash. After 28 days, the samples were crushed and sieved to 9 mm, and were extracted using leaching tests. Composition of geopolymeric and cement (CEM) matrices are shown in Table 3. In all the samples Cr (III) or Cr (VI) were added at a level of 0.5 % by weight, as Cr(NO₃)₃ and K₂Cr₂O₇, respectively.

Table 3.
Composition of S/S matrices

	Proportion by weight (g)					
	Fly Ash	OPC	NaSil	KSil	NaOH 8M	KOH 8M
FA.NaOH 8M (Cr III)	1				0,25	
FA.NaSil NaOH (Cr III)	1		0,57		0,10	
FA.KOH 8M (Cr III)	1					0,22
FA.KSil KOH (Cr III)	1			0,57		0,30
CEM.NaSilNaOH (Cr III)		1	1,14		0,20	
CEM.FA.NaSilNaOH (Cr III)	1	1	2,29		0,40	
FA.NaOH 8M (Cr VI)	1				0,24	
FA.NaSil NaOH (Cr VI)	1		0,57		0,10	
FA.KOH 8M (Cr VI)	1					0,26
FA.KSil KOH (Cr VI)	1			0,57		0,30
CEM.NaSilNaOH (Cr VI)		1	1,14		0,20	
CEM.FA.NaSilNaOH (Cr VI)	1	1	2,29		0,40	

2.3. Compressive strength

A compressive strength test was performed as per ASTM D-1633-84 using two cylinder test samples of each composition and averaging the experimental values obtained. All the samples were tested after 28 days. A Suzpecar, MEM-102 / 50 t, compressive strength testing apparatus was used.

2.4. Leaching tests

The stabilization/solidification efficacy was assessed from a chemical point of view using two leaching tests. The US Environmental Protection Agency (EPA) TCLP (toxicity characteristic leaching procedure) Method No. 1311 test [13] consists of stirring the granular material (< 9 mm), using an acetic acid solution at $\text{pH} = 4.93 \pm 0.05$ with a liquid/solid ratio (L/S) of 20 for 18 h. The UNE-EN 12457 [14] is an extraction method similar to the TCLP, but the extraction fluid is distilled water, in a liquid to solid ratio of 10, for 24 h.

After the tests, samples were filtered through Whatman membrane filters (pore size $0.45 \mu\text{m}$). When the procedures were completed, the total Cr was measured by means of Atomic Absorption Spectrophotometry and Cr^{6+} was analyzed by Spectrophotometry using standard methods [15].

The aim of S/S technology is to obtain solids that reduce the overall environmental impact of waste disposal. To achieve this goal, the USEPA criteria and the EU landfill leachate regulations (European Landfill Directive, EULFD) [16] were followed to establish quality criteria on metal concentration limits in leachates from S/S solids after the usual curing time (28 days).

3. RESULTS AND DISCUSSION

3.1. Compressive strength (CS)

Table 4 shows the compressive strength of S/S solids after 28 days of curing in an oven at $60 \text{ }^\circ\text{C}$ (OVEN) and in the laboratory at $25 \text{ }^\circ\text{C}$ (AMB).

Table 4.
Compressive strength at 28 days.

	CS (MPa)	
	AMB	OVEN
FA.NaOH 8M (Cr III)	6.6	3.8
FA.NaSil NaOH (Cr III)	11.5	16.0
FA.KOH 8M (Cr III)	5.6	3.8

FA.KSiI KOH (Cr III)	32.2	25.2
CEM.NaSiI NaOH (Cr III)	17.5	7.4
CEM.FA.NaSiI NaOH (Cr III)	23.2	29.2
FA.NaOH 8M (Cr VI)	6.6	7.5
FA.NaSiI NaOH (Cr VI)	10.2	18.7
FA.KOH 8M (Cr VI)	2.8	5.9
FA.KSiI KOH (Cr VI)		24.3
CEM.NaSiI NaOH (Cr VI)	19.1	22.1
CEM.FA.NaSiI NaOH (Cr VI)	20.1	24.8

As can be noted, there are no results for Cr (VI)-solids prepared with KSiI KOH cured at ambient temperature because the samples did not set in the 28 day period.

The results show that, in general, compressive strength (CS) values are higher when the S/S solids are cured at 60 °C. On the other hand, for both Cr (VI) and Cr (III) samples, whether in OPC or in FA mixtures, the following results were also observed with regard to the activating solutions used:

- NaOH 8 M solution produces better CS than KOH 8M.
- Silicate samples reach higher CS than hydroxide samples.
- Sodium silicate S/S solids show lower CS than potassium silicate analogues.

The S/S solids containing OPC and FA showed the highest CS values of all the mixtures, followed by FAKSiI KOH solids.

3.2. Leaching tests

3.2.1. UNE-EN 12457 leaching test

Table 5 shows the pH and total chromium concentration values in EN 12457-4 leachates at 28 days.

Table 5.
pH and metal concentrations in UNE-EN 12457 leachates at 28 days

AMB		OVEN	
pH	Cr total (mg/L)	pH	Cr total (mg/L)

FA.NaOH 8M (Cr III)	12.25	5.10	11.4	1.05
FA.NaSil NaOH (Cr III)	12.44	0.25	11.72	0.33
FA.KOH 8M (Cr III)	12.3	7.70	11.46	9.90
FA.KSil KOH (Cr III)	---	---	12.48	0.35
CEM.NaSilNaOH (Cr III)	12.77	4.50	12.72	5.40
CEM.FA.NaSilNaOH (Cr III)	12.73	1,00	12.37	0.66
FA.NaOH 8M (Cr VI)	12.63	832	11.61	728
FA.NaSil NaOH (Cr VI)	12.38	680	11.83	520
FA.KOH 8M (Cr VI)	12.41	920	12.28	872
FA.KSil KOH (Cr VI)	---	---	12.69	528
CEM.NaSilNaOH (Cr VI)	12.7	482	12.55	472
CEM.FA.NaSilNaOH (Cr VI)	12.74	302	12.6	412

The samples analyzed show pH values in EN 12457 leachates at 28 days between 11.4 and 12.77, always being lower in OVEN than AMB samples. Also, it can be clearly appreciated that the Cr leachability is higher in Cr (VI) samples than in Cr (III) samples.

Both, for Cr (VI) and Cr (III) samples, the highest Cr concentrations were leached from S/S solids in which KOH 8M was used as the activating solution. The use of NaOH as an activating solution produces leachates with a lower total chromium concentration than potassium hydroxide.

In general, the utilization of sodium or potassium silicate activating solutions produces lower total chromium leachate concentrations than their respective hydroxide analogues without silicate. The use of potassium or sodium silicate produces similar Cr leachate concentrations. However, the KSil samples present very long setting times at room temperature and this is the reason why ambient-cured samples were not subjected to the EN-12457 test. When OPC is used along with alkaline activators in Cr(VI) samples, the leaching results obtained are better than when fly ash is used with the same activators. The S/S solids prepared with FA.NaSil NaOH (just in Cr (III) samples) and with OPC and fly ash showed the lowest chromium EN-12457 leachability.

Table 6 shows the total chromium leached fractions in the EN 12457-4 leachates, calculated as the percentage between the total chromium concentration in leachates and the total chromium added as Cr (VI) or Cr (III).

Table 6.
Total chromium leached fractions in EN 12457-4 leachates

UNE EN	Cr added (mg)	AMB		OVEN	
		Cr total (mg)	Cr total/Cr added (%)	Cr total (mg)	Cr total/Cr added (%)
FA.NaOH 8M (Cr III)	2000	0.51	0.0255	0.105	0.00525
FA.NaSil NaOH (Cr III)	2000	0.025	0.00125	0.033	0.00165
FA.KOH 8M (Cr III)	2000	0.77	0.0385	0.99	0.0495
FA.KSil KOH (Cr III)	2000			0.035	0.00175
CEM.NaSilNaOH (Cr III)	1000	0.45	0.045	0.54	0.054
CEM.FA.NaSilNaOH (Cr III)	1000	0.1	0.01	0.066	0.0066
FA.NaOH 8M (Cr VI)	2000	83.2	4.16	72.8	3.64
FA.NaSil NaOH (Cr VI)	2000	68,0	3.40	52,0	2.60
FA.KOH 8M (Cr VI)	2000	92,0	4.60	87.2	4.36
FA.KSil KOH (Cr VI)	2000			52.8	2.64
CEM.NaSilNaOH (Cr VI)	1000	48.2	4.82	47.2	4.72
CEM.FA.NaSilNaOH (Cr VI)	1000	30.2	3.02	41.2	4.12

As can be seen, the Cr leached fractions of the chromium (III) mixtures are very low, around 0.021 % in ambient-cured samples, and 0.019 % in oven-cured samples. Conversely, the Cr leached fractions in Cr (VI) samples are much higher, around 3.64 % and 3.51 % in ambient- and oven-cured samples, respectively.

3.2.2. TCLP leaching test

Table 7 shows the pH and the total chromium contents in TCLP leachates at 28 days.

Table 7.
pH and metal concentrations in TCLP leachates at 28 days and USEPA limits

	AMB		OVEN	
	pH	Cr total (mg/L)	pH	Cr total (mg/L)
FA.NaOH 8M (Cr III)	5.03	2.90	4.69	1.37
FA.NaSil NaOH (Cr III)	4.91	0.40	4.43	1.01
FA.KOH 8M (Cr III)	4.72	22.5	4.59	6.90

FA.KSiI KOH (Cr III)			4.76	0.48
CEM.NaSiI NaOH (Cr III)	11.9	1.5	12.2	2.10
CEM.FA.NaSiI NaOH (Cr III)	7.36	0.6	7.61	0.08
FA.NaOH 8M (Cr VI)	5.16	392	4.77	392
FA.NaSiI NaOH (Cr VI)	4.63	384	4.26	288
FA.KOH 8M (Cr VI)	4.60	484	5.16	412
FA.KSiI KOH (Cr VI)			5.08	236
CEM.NaSiI NaOH (Cr VI)	11.9	200	11.9	228
CEM.FA.NaSiI NaOH (Cr VI)	7.23	172	7.62	212
USEPA TCLP		5		5

The leachates of the samples prepared with OPC were alkaline, with pH values between around 12, except the S/S solids prepared using FA plus NaSiI NaOH which presents a neutral pH for any cured condition. However, samples prepared with geopolymeric activators showed a neutral or slightly acidic pH. As can be seen, Cr (VI) was poorly immobilized; all samples exceeded the EPA TCLP limit of 5 mg/L for Cr stabilization. However, Cr (III) was quite well immobilized, except in the FA.KOH S/S solids.

Both for Cr (VI) and Cr (III) samples, the highest concentrations were leached in samples using KOH 8M as the activating solution. Besides, in all cases, the use of sodium hydroxide as an activating solution produced leachates with a lower amount of total chromium than the potassium hydroxide samples.

Moreover, the use of silicate plus alkaline hydroxide instead of hydroxide alone reduced the chromium leaching. As occurred in the EN-12457 leaching study, samples prepared with potassium silicate cured in the oven showed better Cr immobilization than sodium silicate samples.

S/S solids prepared with OPC and fly ash presented lower chromium leachability in Cr (III) and Cr (VI) samples than those prepared with OPC alone. Furthermore, the OPC and fly ash mixtures, which are the only ones that give a TCLP leachate with a neutral pH, showed the lowest chromium leachability of all the mixtures.

Table 8 shows the total chromium leached fractions in the TCLP leachates, calculated as the percentage between the total chromium concentration in leachates and the total chromium added as Cr (VI) or Cr (III).

Table 8.
Total chromium leached fraction in TCLP leachates

TCLP	Cr added (mg)	AMB		OVEN	
		Cr total (mg)	Cr total/Cr added (%)	Cr total (mg)	Cr total/Cr added (%)
FA.NaOH 8M (Cr III)	2000	0.58	0.029	0.274	0.0137
FA.NaSil NaOH (Cr III)	2000	0.08	0.004	0.202	0.0101
FA.KOH 8M (Cr III)	2000	4.5	0.225	1.38	0.069
FA.KSil KOH (Cr III)	2000			0.096	0.0048
CEM.NaSilNaOH (Cr III)	1000	0.3	0.03	0.42	0.042
CEM.FA.NaSilNaOH (Cr III)	1000	0.12	0.012	0.016	0.0016
FA.NaOH 8M (Cr VI)	2000	78.4	3.92	78.4	3.92
FA.NaSil NaOH (Cr VI)	2000	76.8	3.84	57.6	2.88
FA.KOH 8M (Cr VI)	2000	96.8	4.84	82.4	4.12
FA.KSil KOH (Cr VI)	2000			47.2	2.36
CEM.NaSilNaOH (Cr VI)	1000	40	4	45.6	4.56
CEM.FA.NaSilNaOH (Cr VI)	1000	34.4	3.44	42.4	4.24

The same effect described in the EN 12457-4 leachates can be observed here. The leached fraction of chromium (III) is low, around 0.046 % and 0.021 % in ambient- and oven-cured samples, respectively, whereas the average leached proportion of Cr (VI) is much higher, around 3.65 % and 3.48 % in ambient- and oven-cured samples, respectively.

3.2.2. Measurement of Cr (VI) concentrations in leachates

Total chromium and chromium (VI) were measured in leachates in order to calculate the proportion of Cr (VI) reduced to Cr (III) or the proportion of Cr (III) oxidized to Cr (VI). In the Cr (VI) samples Cr (VI) remains as Cr (VI), without being reduced to Cr (III). However, the measurement of Cr (VI) in the mixtures prepared with Cr (III) showed significant concentration values of Cr (VI), which indicate some type of oxidation reaction in the solid that transforms Cr (III) into Cr (VI). The results in EN 12457-4 and TCLP tests are detailed in Table 9 for the Cr (III) samples.

Table 9.
Total chromium and Cr (6+) in TCLP and EN 12457-4 leachates

	AMB	OVEN		AMB	OVEN
--	-----	------	--	-----	------

TCLP	Cr total (mg/L)	Cr +6 (mg/L)	Cr total (mg/L)	Cr+ 6 (mg/L)	EN 12457	Cr total (mg/L)	Cr+ 6 (mg/L)	Cr total (mg/L)	Cr+ 6 (mg/L)
FA.NaOH 8M (Cr III)	2.90	1.26	1.37	0.01	FA.NaOH 8M (Cr III)	5.10	4.39	1.05	0.73
FA.NaSil NaOH (Cr III)	0.40	ND	1.01	ND	FA.NaSil NaOH (Cr III)	0.25	0.11	0.33	0.13
FA.KOH 8M (Cr III)	22.5	2.22	6.90	3.95	FA.KOH 8M (Cr III)	7.70	7.21	9.90	9.16
FA.KSil KOH (Cr III)	---	---	0.48	ND	FA.KSil KOH (Cr III)	---	---	0.35	0.11
CEM.NaSilNaOH (Cr III)	1.50	1.60	2.10	2.33	CEM.NaSilNaOH (Cr III)	4.50	3.89	5.40	5.18
CEM.FA.NaSilNaOH (Cr III)	0.60	0.60	0.08	0.07	CEM.FA.NaSilNaOH (Cr III)	1,00	0.87	0.66	0.58

ND: Non detected

These results are difficult to explain, but in any case lead us to conclude that the alkaline systems studied could favor oxidizing conditions, which would partly transform Cr (III) into Cr (VI). This is an issue that must be taken into account and that is detrimental to the application of these matrices for Cr immobilization.

4. CONCLUSIONS

The present paper describes the immobilization (S/S) of chromium using fly ash-based geopolymer binders and other more conventional S/S systems in simulated waste containing Cr (VI) and Cr (III) ions. The study considers the effect of the composition of the S/S mixture on the compressive strength (CS) of the S/S solids obtained and on the chromium immobilization efficiency. The main compressive strength results obtained in this study can be summarized as follows:

- The higher the cured temperature of the solids, the higher their CS.
- NaOH 8 M activating solution produced S/S solids with higher CS than KOH 8M.
- Silicate-samples reached higher CS than hydroxide samples.
- Sodium silicate-solids showed lower CS than potassium silicate-solids.
- The solids prepared with OPC and FA showed the highest CS values.
- Cr (VI) containing solids prepared with KSilKOH and cured at ambient temperature did not set at 28 days.

The main leaching results are the following:

- There are no significant differences in Cr leachability between the two cured conditions used for S/S solids.
- Cr (III) is oxidized to Cr (VI) in most Cr (III) samples, but the total chromium leached is around 0.1 % of the total Cr (III) added.

- More than 95 % of the total Cr (VI) added is immobilized in the S/S solids.
- Chromium stabilization achieved with OPC alone as S/S binder is better than that achieved with fly ash.
- The use of sodium hydroxide as an activating solution in the S/S mixtures reduces Cr leachability as compared to potassium hydroxide.
- The use of silicate plus alkaline hydroxide instead of hydroxide alone as an activating solution also reduces the chromium leachability.
- The S/S solids prepared with OPC and fly ash showed the lowest chromium leachability.

ACKNOWLEDGMENTS

The authors acknowledge Industrias Químicas del Ebro (Zaragoza, Spain) for supplying the potassium silicate solution used in this work.

REFERENCES

- [1] Davidovits, J. and Comrie, D. in Proceedings of Geopolymer '88 , Compiegne, France, 1988
- [2] Van Jaarsveld, J.G.S., Van Deventer, J.S.J., Lorenzen L. Miner. Eng., 1997, 10 (7), p. 659.
- [3] Davidovits J. In Proceedings First International Conference on Alkaline Cements and Concretes, 1994, pp. 131-149.
- [4] Van Jaarsveld, J.G.S., Van Deventer, J.S.J., Schwartzman, A. Miner. Eng., 1998, 12 (1), p.75.
- [5] Van Jaarsveld, J.G.S., Van Deventer, J.S.J., Lorenzen, L. Metallurgical and Materials Transactions B, 1998, 29, p. 659.
- [6] Perera, D.S., Vance, E.R., Aly, Z., Davis, J., Nicholson, C.L.. 2. Ceramic Transactions, (Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries XI), 2006, 176, p. 91.
- [7] Perera, D.S., Blackford, M.G., Vance, E.R., Hanna, J.V., Finnie, K.S., Nicholson, C.L. Materials Research Society Symposium Proceedings, 2004, 824, pp. 607-612.
- [8] Fernandez Jiminez, A., Lachowski, E.E., Palomo, A., Macphee, D.E. Cement and Concrete Composites, 2004, 26(8), p. 1001.
- [9] Xu, J.Z., Zhou, Y.L., Chang, Q., Qu, H.Q. Materials Letters, 2006, 60(6), p. 820.

- [10] Zhang, J., Provis, J.L., Feng, D., Van Deventer, J.S.J. Journal of Hazardous Materials, 2008, 157, p. 587.
- [11] Palomo, A. and Palacios, M. Cement Concrete Res. 2003, 33 (2), p. 289.
- [12] Deja, J. Cement Concrete Res., 2002, 32 (12), p. 1971.
- [13] US EPA, 1986. Test methods for evaluating solid wastes, toxicity characteristic leaching procedure (TCLP), Method 1311 SW-846, third ed. Environmental Protection Agency, Washington, DC, USA.
- [14] Spanish Standard UNE-EN 12457: Characterisation of waste. Leaching compliance test for leaching of granular waste materials and sludges. 2003
- [15] American Public Health Association (A.P.H.A). Determination of Cr (VI). Standard Methods for the Examination of Water and Wastewater 17th Ed., Washington, DC, 1989
- [16] EULFD. Council Directive 1999/31/EC of 26 April 1999 on the landfill of waste.