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Sequential Extraction for Evaluating the Behaviour of Selected Chemical Elements in Light weight Aggregates Manufactured From Mining and Industrial Wastes

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ABSTRACT: The chemical extraction of twenty-nine elements in a washing aggregate sludge, a clay-rich sediment, a sewage sludge, the mixtures of these materials and the artificial lightweight aggregates (LWAs) manufactured with them was determined by applying the optimized European Community Bureau of Reference sequential extraction procedure in order to establish the effect of the thermal treatment on the extraction of the selected elements. In accordance with the UNE-EN-1744-3 standard (2003), which states a single extraction procedure, preparation of eluates by aggregate leaching was also carried out. All the elements are mainly associated with the residual fraction in the LWAs so their availability is relatively low. The element that presented the highest concentration in the eluates after completion of the single extraction procedure was Fe. All the studied elements are in concentrations below the limit values for *inert wastes* so, from the standpoint of chemical leaching, the studied LWAs may be used in lightweight concrete manufacturing.

Key words: Aggregate sludge, Sediment, Sewage, Lightweight, Fractionation, Extraction ratio, BCR Sequential extraction

INTRODUCTION

In soils, sediments and others substrates, elements can be in different chemical patterns associated with various inorganic and organic phases (Chao, 1984). This chemical fractionation is very important to the potential availability and mobility of the elements (Filgueiras *et al.,* 2004). Sequential extraction procedures (*SEP*) consist on the successive treatment of a matrix, with reagents with an increasing degree of extractability, in different operating conditions. This treatment allows the selective and gradual extraction of the chemical elements of the studied matrix according to their ability to mobilize. Subsequently, element concentrations are measured in each obtained extract, so the quantities of these elements can be established in a decreasing order of mobility and hazard.

In 1992, the use of different extracting agents and their application made that the *Community Bureau of Reference* (the actual *Standards, Measurement and Testing Programme*) finalized to standardize the different schemes with a sequential extraction method, commonly known as *BCR*. There are many types of techniques that may be used to reduce or nullify the toxicity of wastes, such as ceramization or vitrification (Castells, 2000). Artificial lightweight aggregates (LWAs) production from waste materials can be a satisfactory application of the ceramization and/or vitrification techniques. Artificial LWAs are aggregates with a particle density not exceeding 2.00 g/cm^3 and/or with a loose bulk density not exceeding 1.20 g/cm^3 that are obtained after an industrial process with a treatment of the raw material such as the thermal treatment (UNE-EN-13055-1, 2003).

Extraction ratio ($ER_{a,b}$) calculation according to González-Corrochano et al. (2011a) allows evaluating the thermal process effects on the extraction of the analysed elements:

- $ER_{a,b}$ values greater than unity ($ER_{a,b} > 1$) mean a decrease of the element *a* concentration, in the extract (fraction) *b*, of the LWAs with respect to the raw material or a positive effect of the thermal treatment on the extraction of the element *a* that is associated with the fraction *b* of the raw material;
- $ER_{a,b}$ values lower than unity ($ER_{a,b} < 1$) mean a increase of the element *a* concentration, in the extract

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(fraction) *b*, of the LWAs with respect to the raw material or a negative effect of the thermal treatment on the extraction of the element *a* that is associated with the fraction *b* of the raw material;

This study is a part of a more general research work. The other parts have been previously reported in González-Corrochano et al. (2009, 2011a, 2011b).

The objectives were: i) to establish the chemical fractionation of different transition metals (*TMs*), rare earth elements (*REEs*) and other elements (*OEs*) in the raw materials and in the LWAs manufactured with them; ii) to determine the effect of the thermal treatment on the extraction of the element found in the raw materials by the $ER_{a,b}$ calculation; iii) to know the levels of transition metals, rare earth elements and other elements in the eluates obtained from the leaching of the studied LWAs.

MATERIALS & METHODS

Artificial LWAs resulting from a previous study (González-Corrochano *et al.,* 2009) has been selected. These types of LWAs are:

i) W50C50-1200-15. They were manufactured from 50% (wt) of washing aggregate sludge and 50% (wt) of clay-rich sediment (*W50C50* mixture), sintered at 1200ºC for a dwell time of 15 min.

ii) W75S25-1225-15. They were produced with 75% (wt) of washing aggregate sludge and 25% (wt) of sewage sludge (*W75S25* mixture), sintered at 1225ºC for a dwell time of 15 min.

The mineralogical composition of the raw materials was (González-Corrochano et al. (2009): quartz, phyllosilicates and feldspars are present in different proportions in *W* and *C*. *W* also contains calcite and dolomite. *SS* does not contain any crystalline phases. The studied LWAs contain quartz and plagioclases (with mainly anorthitic composition, González-Corrochano *et al.,* 2011b).

The BCR sequential extraction procedure (BCR-SEP) was applied in the raw materials (*W*, *C* and *SS*), in the milled mixtures (*W50C50* and *W75S25*) and in the selected LWAs (*W50C50-1200-15* and *W75S25-1225-15*). The operating conditions and the geochemical fractions obtained are the following (Sahuquillo *et al.,* 1999):

- Step 1: extraction with the *solution A* (0.11 M acetic acid at pH 2.85). 40 ml of the *solution A* were added to 1 g of raw materials/wastes, 1 g of the mixtures and 3 pellets of each type (in triplicate). The elements removed are those that are weakly adsorbed, exchangeable and water- and acid-soluble (F1).
- Step 2: extraction with the *solution B* (0.5 M hydroxylamine hydrochloride at pH 1.5). 40 ml of *solution B* were added to the residue from the previous step.. During this step, the reducible fraction, such as Fe-Mn (hydr)oxide-bound elements, is extracted (F2).
- Step 3: reaction with the *solution C* (8.8 M H_2O_2) followed by extraction with the *solution D* (1.0 M ammonium acetate at pH 2). 10 ml of *solution C* were added to the residue from the previous step. It was left to react at room temperature for one hour and then it was heated at 85ºC until the 8.8 M H_2O_2 volume was reduced. Finally, 50 ml of *solution D* were added to the residue. Oxidizable elements, such as the sulphide- and organic-matter-bound fraction, are the extracted elements in this stage (F3).
- Step 4: pseudo-total digestion. 0.5 g of the residue obtained in step 3 was digested with 9 ml of concentrated HNO_3 + 3 ml of concentrated HCl, in a microwave unit (CEM, *MarsXpress*) in accordance with EPA procedure 3051A (USEPA, 1995). Most elements are removed during this step (F4 or residual fraction), but other elements, primarily resistant phases that are not dissolved in the aqua regia solution, remain unremoved, forming part of the undigested material.

The availability of the elements decreases in the order: F1 > F2 > F3 > F4 (Ma and Rao, 1997). The concentration that can be released under specific environmental conditions is the sum of F1, F2 and F3 ("1+2+3 or "non-residual fraction"). The elements that cannot be released under the environmental conditions found in nature are considered those associated with F4 (Dang *et al.,* 2002). The sum of the concentrations associated with F1, F2, F3 and F4 ("1+2+3+4) is also called "pseudo-total concentration", since the elements in the undigested phases are not included.

The concentrations of twenty-nine elements (transition metals, rare earth elements and others) in F1, F2, F3 and F4 were analysed by inductively coupled plasma-mass spectroscopy (ICP-MS, Thermo Electron, *XSeriesII*).

The $ER_{a,b}$ has been calculated following the equation (González-Corrochano *et al.,* 2011a):

$$ER_{a,b} = \frac{[mixture_{a,b}]}{[LWA_{a,b}] * \left(1 - \frac{LOI}{100}\right)} \qquad (1)$$

Where:

- $[mixture_{a,b}]$ and $[LWA_{a,b}]$ are the concentrations (mg/kg), of the element *a*, in the fraction *b*, in the mixture and in the LWAs, respectively;
- *LOI* is the loss on ignition (%) of the mixtures during the production of the LWAs. 10.68% and 24.26% have been the LOI values of *W50C50* and *W75S25*, respectively (González-Corrochano *et al.,* 2009).

Eluates by aggregate leaching were obtained in accordance with the UNE-EN-1744-3 standard (2003), which consists of placing the LWAs on a grid and introducing them into a tank, where they are subjected to leaching with ultrapure water for 24 h (± 10 min). The liquid:solid ratio (wt) used was 20:1 and the samples were tested in triplicate. After the leaching time, the eluates were filtered through 45-µm membrane filters and, as in the case of the extracts resulting from the BCR-SEP, the contents of the twenty-nine elements were measured by ICP-MS (Thermo Electron, *XSeriesII*).

RESULTS & DISCUSSION

Results and discussion are presented below separating the studied elements in three groups: *i)* transition metals (*TMs*); *ii)* rare earth elements (*REEs*) and; *iii)* others elements (*OEs*). The studied transition metals (Ti, Mn, Fe, Co, Mo, Ag) are mainly associated with the residual fraction of the raw materials, with the exceptions of Ag, which could be mainly associated with the reducible and oxidizable fractions of *W* and *C*, respectively (64.82% and 66.03%, Tables 1 and 2), and Mo, which could be primarily bound to the oxidizable fraction in *SS* (70.35%, Table 3).

Mn, in *W* and *C*, and Fe, in *SS*, present the highest concentrations associated with F1 (Tables 1-3); therefore, these elements will be the most available when changes in pH occur. When changes occur in the redox and the (pH + redox) conditions of the raw materials, Fe will be the element with the highest available concentration, since it presents the highest “F2+F3 and non-residual concentrations, respectively (Tables 1-3). The availability of all the studied transition metals in the LWAs is relatively low, since they are mainly associated (76.36%-100%) with the residual fraction in both types of LWAs. The behavior of Co and Mo has been given special attention, since these elements are considered to be “toxic” in US, European and Spanish regulations. The pseudo-total concentrations of Co decrease after the thermal treatment in both types of LWAs ($ER_{Co,\text{©}1+2+3+4}$=2.33, Fig. 1a; $ER_{Co,\text{©}1+2+3+4}$=2.04, Fig. 2a). This may be due to the fact that this element becomes a part of the undigested material in the LWAs, since volatilization of Co is not possible (boiling point of Co H” 2900ºC >> heating temperatures). The undigested material may be composed of neo-formed phases created during the heating process of the LWAs, i.e. plagioclases (González-Corrochano *et al.*, 2011b), LWA matrix (amorphous/vitrified material) and other minerals in quantities undetectable by XRD. In the undigested material, Co may be found in the vitrified/amorphous matrix, since the presence of Co in aluminosilicate melts has been reported (Keppler and Bagdassarov, 1999).

Despite the decrease in the pseudo-total concentrations, an increase in the adsorbed, exchangeable and water- and acid-soluble Co occurs in *W50C50-1200-15* ($ER_{Co,F1}$=0.24, Fig. 2a). This is due to geochemical changes of Co associated to F2, F3 or F4 in the raw material since its concentrations decrease after the thermal treatment (Fig. 2a). Therefore, special care should be taken when the raw materials of LWAs present high Co concentrations, even when they are mainly associated to the residual fraction. The “1+2+3+4 concentrations of Mo in both types of LWAs also decrease after the ceramic process with respect to the original mixtures ($ER_{Mo,\text{”}1+2+3+4}$=1.77, Fig. 1b; $ER_{Mo,\text{”}1+2+3+4}$=4.01, Fig. 2b). Moreover, it may be observed that the concentration of the oxidizable fraction increases after the thermal treatment in *W50C50-1200-15* ($ER_{Mo,F3}$=0.00, Fig. 2b). Consequently, if this type of LWA is exposed to oxidizing conditions, Mo will be more available than in the raw materials.

A comparison between the limit values for inert wastes, specified in Decision 2003/33/EC (European Council, 2003), and the results obtained has been carried out in Table 4. In both types of LWAs, Mo is found in concentrations below the limits specified in Decision 2003/33/EC (European Council, 2003) for *inert wastes* (Table 4).

The REE with the highest pseudo-total-concentration in the raw materials is Ce (Tables 1, 2 and 3). Especially in the case of *W* and *C*, this is due to the fact that this element is the most abundant REE in the earth’s crust (average abundance of 66 mg/kg; Tyler, 2004). Cerium is the REE with the highest concentration associated with the F1 (adsorbed, exchangeable, water- and acid-soluble fraction) in *W* (1.66 mg/kg; Table 1) and in *C* (0.97 mg/kg; Table 2). In SS, it is La (1.40 mg/kg; Table 3). As consequence, when changes in ph occur in the ponds and/or landfills, these elements are the REEs which exhibit the highest available quantities.

As in the previous fraction, Ce, in the washing aggregate sludge and in the clay-rich sediment, and La, in the sewage sludge, are the REEs with the highest concentrations associated with the sum of F2 and F3 (reducible and oxidizable fractions, respectively; Tables 1, 2 and 3) so these elements are the REEs which exhibit the highest available concentrations if changes in the redox conditions occur. Thus, when ponds of *W* and/or landfills are soaked by rainwater and then dried, Ce and La may be released to the environment since the major changes in the behavior of redox-controlled trace elements typically occur at the interface between water and the solid phase (this interface marks the change from an anoxic to an oxic medium; Schlieker *et al.*, 2001). Depending on the raw materials, the REEs are mainly

Table 1. Concentrations (mg/kg) of the studied elements associated with the geochemical fractions in the washing aggregate sludge. Bold, italic and underlined = Fraction to which the element is mainly associated. In brackets = pseudo-total concentration percentage. - - - = Below the detection limit. n.d. = not determined

Raw material		**WASHING AGGREGATE SLUDGE (*W*)**					
Geochemical Fraction		**1**	**2**	**3**	**4**	**Σ 1+2+3**	**Σ 1+2+3+4**
Element (mg/kg)		**(Exchangeable, soluble)**	**(Reducible)**	**(Oxidizable)**	**(Residual)**	**(Non-residual)**	**(Pseudo-total)**
Transition Metals (TMs)	**Ti**	0.63 (0.09)	1.95 (0.28)	32.70 (4.68)	**663.29 (94.95)**	35.28 (5.05)	698.57
	Mn	127.91 (28.56)	135.79 (30.32)	12.43 (2.78)	**171.71 (38.34)**	276.14 (61.66)	447.85
	Fe	0.11 (0.00)	582.98 (2.07)	326.03 (1.16)	**27203.93 (96.77)**	909.24 (3.23)	28113.17
	Co	0.27 (2.95)	2.56 (27.89)	0.32 (3.45)	**6.04 (65.71)**	3.15 (34.29)	9.20
	Mo	0.07 (20.25)	- - -	- - -	**0.27 (79.75)**	0.07 (20.25)	0.34
	Ag	- - -	**0.07 (64.82)**	0.04 (35.18)	- - -	0.11 (100)	0.11
Rare Earth Elements (REEs)	**La**	0.88 (3.33)	4.79 (18.15)	0.58 (2.20)	**20.17 (76.33)**	6.25 (23.67)	26.42
	Ce	1.66 (3.02)	12.67 (23.05)	1.72 (3.14)	**38.93 (70.80)**	16.06 (29.20)	54.99
	Pr	0.21 (3.40)	1.42 (22.67)	0.18 (2.95)	**4.43 (70.98)**	1.81 (29.02)	6.25
	Nd	1.10 (4.46)	6.01 (24.33)	0.83 (3.37)	**16.77 (67.83)**	7.95 (32.17)	24.72
	Sm	0.24 (4.79)	1.46 (29.28)	0.21 (4.30)	**3.08 (61.63)**	1.91 (38.37)	4.99
	Eu	0.04 (5.33)	0.33 (40.46)	0.03 (3.25)	**0.41 (50.96)**	0.40 (49.04)	0.81
	Gd	0.27 (6.03)	1.53 (33.98)	0.20 (4.44)	**2.50 (55.55)**	2.00 (44.45)	4.50
	Tb	0.02 (4.42)	0.23 (43.62)	- - -	**0.27 (51.96)**	0.25 (48.04)	0.52
	Dy	0.15 (5.15)	**1.30 (44.54)**	0.17 (5.99)	1.29 (44.31)	1.62 (55.69)	2.92
	Ho	0.02 (5.02)	**0.23 (50.00)**	- - -	0.21 (44.98)	0.25 (55.02)	0.46
	Er	0.07 (5.58)	**0.61 (46.51)**	0.08 (6.32)	0.54 (41.58)	0.76 (58.42)	1.31
	Tm	- - -	**0.08 (67.57)**	- - -	0.04 (32.43)	0.08 (67.57)	0.12
	Yb	0.05 (4.87)	**0.48 (44.89)**	0.08 (7.61)	0.45 (42.63)	0.61 (57.37)	1.06
	Lu	- - -	**0.06 (100.00)**	- - -	- - -	0.06 (100)	0.06
	Y	1.09 (7.77)	**6.39 (45.77)**	0.76 (5.42)	5.73 (41.04)	8.24 (58.96)	13.97
Other Elements	**Th**	- - -	- - -	0.06 (0.83)	**7.72 (99.17)**	0.06 (0.83)	7.79
	U	0.06 (4.19)	0.34 (23.69)	0.18 (12.72)	**0.85 (59.39)**	0.58 (40.61)	1.43
	Be	- - -	0.43 (22.60)	0.15 (7.72)	**1.33 (69.68)**	0.58 (30.32)	1.91
	As	0.71 (5.01)	1.28 (9.03)	0.14 (1.01)	**12.06 (84.94)**	2.14 (15.06)	14.20
	Se	- - -	0.16 (4.34)	- - -	**0.20 (55.66)**	0.16 (44.34)	0.36
	Sr	**113.99 (77.50)**	17.27 (11.74)	0.90 (0.62)	14.92 (10.14)	132.17 (89.86)	147.09
	Sb	- - -	- - -	- - -	**0.53 (100.00)**	n.d.	0.53
	Ba	36.42 (13.01)	**189.64 (67.74)**	5.86 (2.09)	48.02 (17.15)	231.92 (82.85)	279.94

Table 2. Concentrations (mg/kg) of the studied elements associated with the geochemical fractions in the clay-rich sediment. Bold, italic and underlined = Fraction to which the element is mainly associated. In brackets = pseudo-total concentration percentage. - - - = Below the detection limit. n.d. = not determined

Raw material		CLAY-RICH SEDIMENT (*C*)					
Geochemical Fraction		1	2	3	4	Σ 1+2+3	Σ 1+2+3+4
Element (mg/kg)		(Exchangeable, soluble)	(Reducible)	(Oxidizable)	(Residual)	(Non-residual)	(Pseudo-total)
Transition Metals(TMs)	Ti	0.47 (0.04)	---	68.05 (5.93)	**1078.90 (94.03)**	68.52 (5.97)	1147.42
	Mn	9.58 (1.32)	148.20 (20.50)	37.21 (5.15)	**528.05 (73.03)**	194.98 (26.97)	723.03
	Fe	---	996.41 (1.51)	227.23 (0.34)	**64767.48 (98.15)**	1223.64 (1.85)	65991.12
	Co	0.04 (0.24)	2.58 (14.31)	0.67 (3.74)	**14.73 (81.71)**	3.30 (18.29)	18.03
	Mo	---	---	---	**0.41 (100)**	n.d.	0.41
	Ag	---	---	**0.14 (66.03)**	0.07 (33.97)	0.14 (66.03)	0.21
Rare Earth Elements (REEs)	La	0.41 (1.16)	8.85 (25.28)	0.63 (1.81)	**25.12 (71.76)**	9.88 (28.24)	35.00
	Ce	0.97 (1.32)	23.30 (31.72)	1.23 (1.67)	**47.97 (65.29)**	25.50 (34.71)	73.47
	Pr	0.14 (1.56)	2.55 (29.45)	0.19 (2.14)	**5.79 (66.84)**	2.87 (33.16)	8.66
	Nd	0.63 (1.90)	10.40 (31.17)	0.78 (2.34)	**21.55 (64.60)**	11.81 (35.40)	33.36
	Sm	0.16 (2.45)	2.46 (36.66)	0.19 (2.77)	**3.91 (58.12)**	2.81 (41.88)	6.72
	Eu	0.01 (1.07)	0.43 (40.29)	---	**0.63 (58.65)**	0.45 (41.35)	1.08
	Gd	0.18 (3.05)	2.44 (42.27)	0.19 (3.25)	**2.97 (51.43)**	2.81 (48.57)	5.78
	Tb	---	**0.35 (51.41)**	---	0.33 (48.59)	0.35 (51.41)	0.68
	Dy	0.12 (3.38)	**1.84 (50.10)**	0.17 (4.49)	1.54 (42.04)	2.13 (57.96)	3.68
	Ho	---	**0.32 (54.47)**	---	0.27 (45.53)	0.32 (54.47)	0.59
	Er	0.07 (3.88)	**0.81 (47.61)**	0.09 (5.11)	0.74 (43.40)	0.96 (56.60)	1.70
	Tm	---	**0.10 (50.52)**	---	0.10 (49.98)	0.10 (50.52)	0.20
	Yb	0.05 (3.97)	0.59 (43.39)	0.74 (5.48)	**0.64 (47.16)**	0.72 (52.84)	1.36
	Lu	---	0.08 (46.32)	---	**0.09 (53.68)**	0.08 (46.32)	0.17
	Y	0.62 (3.63)	**8.45 (49.15)**	0.81 (4.70)	7.31 (42.52)	9.89 (57.48)	17.20
Other Elements	Th	---	0.16 (1.62)	0.07 (0.71)	**9.37 (97.67)**	0.22 (2.33)	9.59
	U	0.34 (6.00)	**2.85 (50.15)**	0.76 (13.35)	1.73 (30.50)	3.94 (69.50)	5.67
	Be	0.08 (2.45)	0.39 (12.15)	0.30 (9.27)	**2.45 (76.14)**	0.77 (23.86)	3.22
	As	3.86 (10.92)	2.23 (6.33)	1.52 (4.32)	**27.69 (78.43)**	7.61 (21.57)	35.31
	Se	---	0.37 (39.85)	0.05 (5.81)	**0.51 (54.34)**	0.43 (45.66)	0.94
	Sr	**21.94 (45.16)**	11.28 (23.21)	0.95 (1.95)	14.42 (29.67)	34.17 (70.33)	48.59
	Sb	---	---	---	**0.70 (100)**	n.d.	0.70
	Ba	2.44 (2.14)	41.03 (36.06)	---	**70.32 (61.80)**	43.47 (38.20)	113.79

Table 3. Concentrations (mg/kg) of the studied elements associated with the geochemical fractions in the sewage sludge. Bold, italic and underlined = Fraction to which the element is mainly associated. In brackets = pseudo-total concentration percentage. - - - = Below the detection limit. n.d. = not determined

Raw material		**SEWAGE SLUDGE (*SS*)**					
Geochemical Fraction		**1**	**2**	**3**	**4**	**Σ 1+2+3**	**Σ 1+2+3+4**
Element (mg/kg)		**(Exchangeable, soluble)**	**(Reducible)**	**(Oxidizable)**	**(Residual)**	**(Non-residual)**	**(Pseudo-total)**
Transition Metals(TMs)	**Ti**	---	---	20.48 (3.65)	**541.09 (96.35)**	20.48 (3.65)	561.57
	Mn	88.98 (29.60)	33.93 (11.29)	27.78 (9.24)	**149.95 (49.88)**	150.69 (50.12)	300.64
	Fe	172.69 (0.61)	802.53 (2.83)	1021.91 (3.60)	**26378.56 (92.96)**	1997.12 (7.04)	28375.68
	Co	0.46 (4.73)	0.36 (3.71)	0.88 (9.09)	**8.00 (82.48)**	1.70 (17.52)	9.70
	Mo	---	---	**3.79 (70.35)**	1.60 (29.65)	3.79 (70.35)	5.39
	Ag	---	1.21 (12.84)	0.59 (6.21)	**7.63 (80.94)**	1.80 (19.06)	9.43
Rare Earth Elements (REEs)	**La**	1.40 (8.55)	2.03 (12.40)	3.25 (19.82)	**9.71 (59.23)**	6.68 (40.77)	16.39
	Ce	0.77 (3.46)	1.20 (5.40)	3.27 (14.76)	**16.93 (76.38)**	5.24 (23.62)	22.17
	Pr	0.09 (3.34)	0.11(4.10)	0.38 (14.61)	**2.03 (77.94)**	0.57 (22.06)	2.60
	Nd	0.33 (3.36)	0.38 (3.81)	1.56 (15.76)	**7.65 (77.07)**	2.27 (22.93)	9.92
	Sm	0.07 (3.22)	0.07 (3.18)	0.38 (18.42)	**1.54 (75.18)**	0.51 (24.82)	2.04
	Eu	---	---	0.10 (26.75)	**0.27 (73.25)**	0.10 (26.75)	0.38
	Gd	0.07 (3.70)	0.08 (4.54)	0.38 (20.53)	**1.32 (71.23)**	0.53 (28.77)	1.86
	Tb	---	---	0.06 (24.09)	**0.18 (75.91)**	0.06 (24.09)	0.24
	Dy	---	0.08 (5.54)	0.33 (24.17)	**0.96 (70.29)**	0.41 (29.71)	1.37
	Ho	---	---	0.06 (26.30)	**0.17 (73.70)**	0.06 (26.30)	0.24
	Er	---	---	0.17 (26.08)	**0.48 (73.92)**	0.17 (26.08)	0.65
	Tm	---	---	---	---	n.d.	n.d.
	Yb	---	---	0.14 (24.18)	**0.42 (75.82)**	0.14 (24.18)	0.56
	Lu	---	---	---	---	n.d.	n.d.
	Y	0.29 (3.92)	0.68 (9.33)	1.60 (21.98)	**4.72 (64.77)**	2.57 (35.23)	7.28
Other Elements	**Th**	0.11 (3.74)	0.05 (1.66)	0.30 (9.93)	**2.57 (84.67)**	0.47 (15.33)	3.03
	U	1.54 (1.67)	1.07 (1.16)	**48.57 (52.30)**	41.67 (44.88)	51.19 (55.12)	92.86
	Be	---	0.07 (3.85)	0.15 (7.97)	**1.66 (88.18)**	0.22 (11.82)	1.88
	As	0.33 (0.34)	0.74 (0.78)	17.18 (18.01)	**77.14 (80.87)**	18.25 (19.13)	95.39
	Se	0.07 (3.63)	---	0.87 (43.97)	**1.04 (52.40)**	0.94 (47.60)	1.98
	Sr	**326.19 (47.52)**	113.03 (16.47)	185.40 (27.01)	61.76 (9.00)	624.62 (91.00)	686.38
	Sb	---	---	0.26 (19.79)	**1.03 (80.21)**	0.26 (19.79)	1.29
	Ba	**59.14 (38.49)**	32.23 (20.98)	14.08 (9.16)	48.21 (31.37)	105.46 (68.63)	153.67

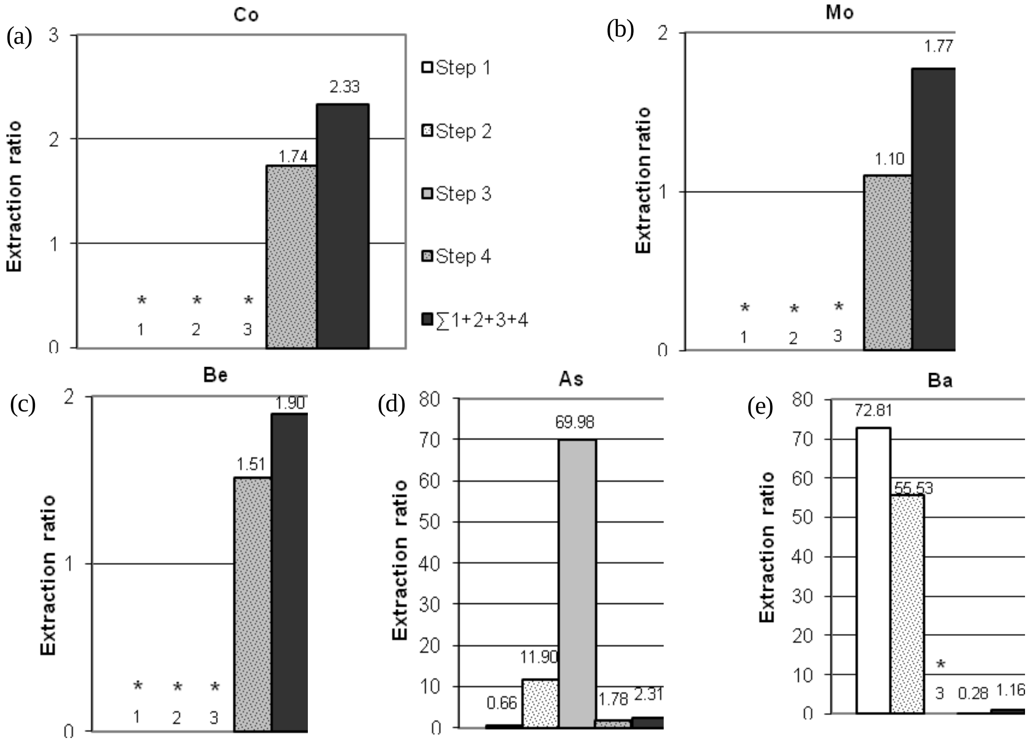

Fig. 1 ***$ER_{a,b}$*** **between** ***W75S25*** **mixture/*W75S25-1225-15 LWA*. a) Co; b) Mo; c) Be; d) As; e) Ba. (*): Concentration in the LWAs is below the detection limit in this fraction (number)**

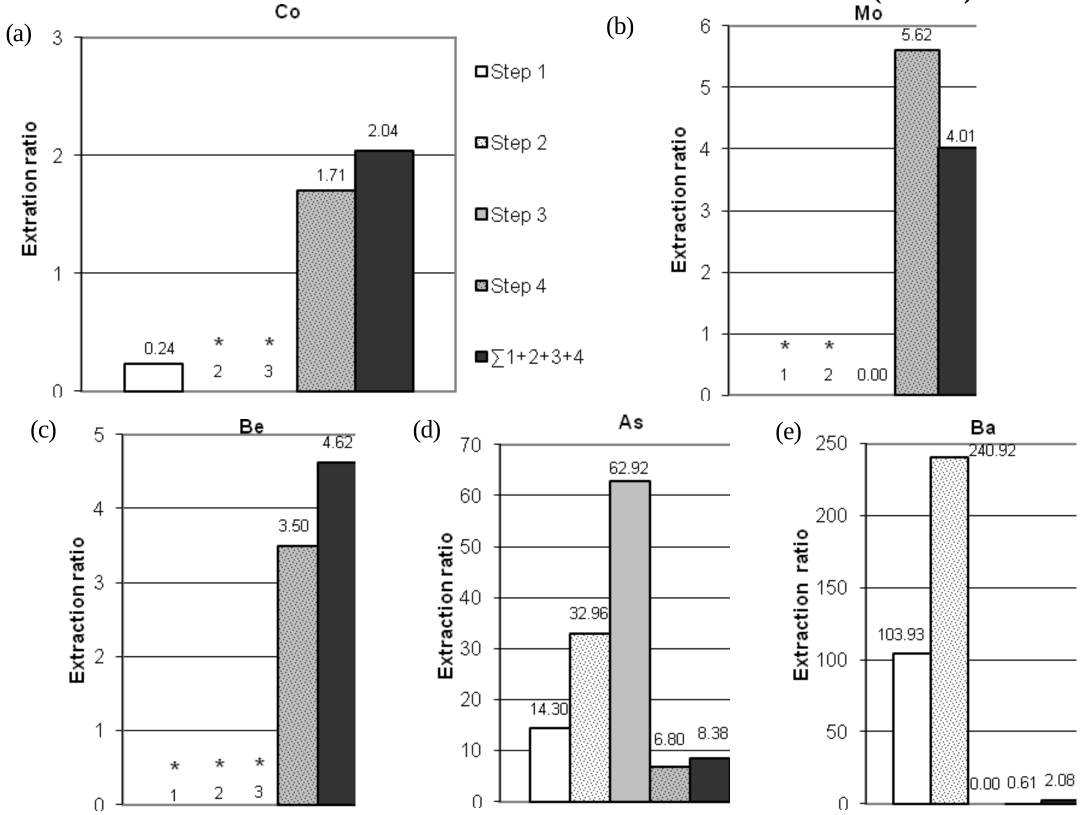

Fig. 2. ***$ER_{a,b}$*** **between** ***W50C50*** **mixture/*W50C50-1200-15 LWAs*. a) Co; b) Mo; c) Be; d) As; e) Ba. (*): Concentration in the LWAs is below the detection limit in this fraction (number)**

Table 4. Concentrations in the eluates and comparison with the limit values for *inert wastes* (according to Decision 2003/33/CE). - - - = Below the detection limit. n.e = not established

LWAs		W75S25-1225-15	W50C50-1200-15	Limit values for *inert wastes* (mg/kg)$^{(b)}$
Element (mg/kg)$^{(a)}$				
Transition Metals (TMs)	**Ti**	0.16	0.07	n.e
	Mn	0.82	0.15	n.e
	Fe	3.77	6.67	n.e
	Co	0.02	0.01	n.e
	Mo	0.04	---	**0.5**
	Ag	---	---	n.e
Rare Earth Elements (REEs)	**La**	0.59	0.08	n.e
	Ce	1.06	0.18	n.e
	Pr	0.14	0.02	n.e
	Nd	0.53	0.09	n.e
	Sm	0.10	0.02	n.e
	Eu	0.02	---	n.e
	Gd	0.10	0.02	n.e
	Tb	0.01	---	n.e
	Dy	0.08	0.01	n.e
	Ho	0.01	---	n.e
	Er	0.04	0.01	n.e
	Tm	---	---	n.e
	Yb	0.03	---	n.e
	Lu	---	---	n.e
	Y	0.39	0.07	n.e
Other Elements	**Th**	---	---	n.e
	U	0.03	---	n.e
	Be	0.05	---	n.e
	As	0.49	0.14	**0.5**
	Se	---	---	**0.1**
	Sr	0.75	0.08	n.e
	Sb	---	0.05	**0.06**
	Ba	0.33	---	**20**

(a) Liquid:solid ratio (wt) is 20:1

(b) If the liquid:solid ratio is 10:1

associated with F2 or with F4. Thus, in *W*, the HREEs (Dy-Lu and Y) are primarily associated with F2, while the LREEs and MREEs are associated with F4 (Table 1). In *C*, the LREEs, MREEs (La-Gd), Yb and Lu, are associated with F4 while the rest of REEs are primarily associated with F2 (Table 2). All the REEs are primarily bound to the F4 of *SS* (Table 3). All the REEs are mainly associated (95.53%-100%) with F4 in both types of LWAs.

In the LWAs manufactured with *W* and *SS*, the thermal treatment produces a decrease in the $\Sigma1+2+3$ concentrations of all the REEs (Table 5). These elements have become a part of the undigested material, since their boiling points are higher (1400ºC-3500ºC) than the heating temperature used. In the case of the HREEs, a proportion of the $\Sigma1+2+3$ concentrations could also have become part of the residual fraction since it increases after thermal treatment ($ER_{HREEs,F4}<1$, Table 5).

The heating process also causes a decrease in the $\Sigma1+2+3$ concentrations of all the REEs in the LWAs produced with *W* and *C*, with respect to *W50C50* mixture, since the $ER_{REEs,"1+2+3}$ values are greater than unity (Table 5). These elements have become a part of the undigested material since they neither have volatilized nor have become part of the F4 (except in the case of Lu, the residual fraction also decreases after the heating process: $ER_{REEs,F4}>1$, Table 5).

The extraction with water produces very low quantities of all the REEs (Table 4); Tm and Lu present undetectable levels in the eluates obtained from both

Table 5. Extraction ratio ($ER_{a,b}$), for each studied element, in the non-residual (“1+2+3) and in the residual fraction (F4). Bold, italic and underlined = $ER_{a,b}$ <1. In brackets = concentration difference (mg/kg) between mixtures and lightweight aggregates. n.d = not determined because concentrations in the mixtures and in the lightweight aggregates are below the detection limit

LWAs		***W75S25-1225-15***		***W50C50-1200-15***	
$ER_{a,b}$		**1.00 kg mixture / 0.76 kg LWA(a)**		**1.00 kg mixture / 0.89 kg LWA(b)**	
Fraction		**? 1+2+3**	**F4**	**∑1+2+3**	**F4**
Transition Metals (TMs)	**Ti**	**0.52 (+11.53)**	1.20 (-96.28)	19.96 (-49.49)	3.80 (-663.48)
	Mn	73.15 (-255.73)	**0.97 (+5.34)**	151.91 (-189.27)	2.45 (-182.36)
	Fe	4.95 (-698.49)	2.22 (-16528.26)	20.34 (-887.10)	2.84 (-27528.58)
	Co	>1 (-2.61)	1.74 (-3.32)	5.78 (-2.21)	1.71 (-3.66)
	Mo	>1 (-0.50)	1.10 (-0.07)	**0.00 (+0.02)**	5.62 (-0.20)
	Ag	>1 (-1.80)	**0.76 (+0.17)**	4.61 (-0.10)	**0.00 (+0.18)**
Rare Earth Elements (REEs)	**La**	21.21 (-5.67)	1.73 (-8.12)	62.30 (-7.79)	3.03 (-13.51)
	Ce	22.32 (-10.85)	1.74 (-16.43)	75.20 (-19.80)	2.98 (-26.02)
	Pr	29.77 (-1.37)	1.74 (-1.93)	91.58 (-2.29)	3.07 (-3.14)
	Nd	23.09 (-5.71)	1.69 (-6.81)	64.35 (-9.40)	3.24 (-12.00)
	Sm	36.06 (-1.38)	1.54 (-1.11)	86.70 (-2.19)	2.65 (-1.93)
	Eu	>1 (-0.33)	1.09 (-0.04)	>1 (-0.36)	2.39 (-0.25)
	Gd	39.37 (-1.45)	1.31 (-0.59)	86.92 (-2.29)	2.29 (-1.25)
	Tb	>1 (-0.21)	1.11 (-0.03)	>1 (-0.30)	2.14 (-0.14)
	Dy	>1 (-1.27)	**0.95 (+0.08)**	230.82 (-1.87)	2.15 (-0.69)
	Ho	>1 (-0.23)	**0.84 (+0.04)**	>1 (-0.29)	1.94 (-0.11)
	Er	>1 (-0.60)	**0.78 (+0.17)**	>1 (-0.88)	1.93 (-0.29)
	Tm	>1 (-0.04)	**0.74 (+0.03)**	>1 (-0.10)	1.37 (-0.02)
	Yb	>1 (-0.45)	**0.73 (+0.18)**	>1 (-0.67)	1.93 (-0.24)
	Lu	n.d	**0.00 (+0.10)**	>1 (-0.07)	**0.00 (+0.03)**
	Y	31.09 (-6.42)	**0.77 (+1.83)**	59.50 (-8.85)	1.92 (-2.93)
Other Elements	**Th**	1.31 (-0.01)	2.84 (-5.31)	16.17 (-0.14)	4.50 (-5.59)
	U	61.89 (-11.97)	1.41 (-2.61)	>1 (-2.23)	3.19 (-0.76)
	Be	>1 (-0.45)	1.51 (-0.60)	>1 (-0.63)	3.50 (-1.40)
	As	22.81 (-7.48)	1.78 (-10.43)	25.91 (-4.96)	6.80 (-12.90)
	Se	>1 (-0.43)	1.64 (-0.20)	>1 (-0.33)	3.64 (-0.32)
	Sr	97.90 (-256.22)	**0.06 (+202.04)**	113.83 (-92.38)	**0.20 (+57.11)**
	Sb	n.d	7.79 (-0.69)	**0.00 (+0.06)**	**0.00 (+0.08)**
	Ba	82.18 (-198.07)	**0.28 (+161.04)**	149.40 (-149.84)	**0.61 (+39.25)**

(a) LOI = 24.26% (González-Corrochano et al., 2009)

(b) LOI = 10.68% (González-Corrochano et al., 2009) types of LWAs. The concentrations of all the REEs are lower in *W50C50-1200-15* than in *W75S25-1225-15* (Table 4). In the washing aggregate sludge, Sr and Ba are mainly associated with F1 and F2, respectively, while Th, U, Be, As, Se and Sb are mainly associated with F4 (Table 1). The bulk mineralogy of *W* shows 20%-40% calcite ($CaCO_3$) and 1%-20% dolomite ($CaMg(CO_3)_2$) (González-Corrochano *et al.*, 2009). In this waste, Sr may be predominantly found in the form of strontium carbonate, since isomorphous substitution into the calcium sites occurs in carbonate minerals (Davidson et al. 2005). In the *C*, all the elements are mainly associated with the residual fraction, with the exception of U and Sr (Table 2). In the *SS*, all the elements are also primarily bound to F4, except for U, Sr and Ba (Table 3). The relatively high concentrations of Sr that are adsorbed, exchangeable or water- and acid-soluble in the raw materials (Tables 1, 2 and 3) do not entail significant environmental risks, since this element is not considered to be "toxic" in the various regulations on the matter (Castells, 2000). Ba, in the washing aggregate sludge and the clay-rich sediment, and Sr, in the sewage sludge, present the highest concentrations associated with F2 (189.64 mg/kg, 41.03 mg/kg and 113.03 mg/kg, respectively). In *W*, *C* and *SS* the highest quantities associated with F3 are shown by Ba (5.86 mg/kg), As (1.52 mg/kg) and Sr (185.40 kg/mg), respectively (Tables 1, 2 and 3). Consequently, when changes in the redox conditions occur in the environment of the raw materials, Ba and Sr will be the elements with the highest available concentrations. As regards barium, this fact could entail environmental risks, because the World Health Organization reports that health effects resulting from chronic exposure to Ba include kidney damage and hypertension (Fawell and Mascarenhas, 2004).In Spain, there is no legislation on the use of *W*, *C* and/or *SS* in the manufacturing of artificial LWAs so the maximum levels established in other European countries for the re-use of certain materials as building materials (Cappuyns and Swennen, 2009) have been compared to the obtained results. It is worth noting that As in *W* (14.20 mg/kg, Table 1), *C* (35.31 mg/kg, Table 2) and *SS* (95.39 mg/kg, Table 3) does not exceed the established limit for re-use as a raw material in building materials (200 mg/kg) so the studied materials may be used for the production of LWAs. All the other studied elements are mainly associated (58.70%-100%) with F4 in both types of LWAs. Since Be, As and Ba are considered to be "toxic" in various regulations, particular attention has been given to their behavior after the thermal treatment.

The heating process causes the decrease of the Be associated with the non-residual fraction in both types of LWAs with respect to the initial mixtures (Figs. 1c and 2c). It is also worth noting that the concentrations of residual Be also decrease after the thermal treatment ($ER_{Be,F4}$=1.51 and $ER_{Be,F4}$=3.50; Figs. 1c and 2c). Due to the high boiling point of Be (approximately 3000ºC), volatilization of this element is not possible; therefore, these geochemical forms have become a part of the undigested material. Beryllium atom substitution in the crystalline structure of plagioclases has not been reported (Deer *et al.*, 1992); therefore, Be may be primarily found associated with the amorphous/vitrified material of the LWAs or with minerals in quantities undetectable by XRD.

The concentrations of As bound to F4 decrease when the thermal treatment is applied to *W75S25* and to *W50C50* mixtures (Figs. 1d and 2d). However, the concentration of arsenic associated with the adsorbed, exchangeable and soluble fraction increases in *W75S25-1225-15* ($ER_{As,F1}$=0.66; Fig. 1d). This transformation of residual As into more mobile geochemical forms is a common consequence of the exposure of As-bearing materials to high temperatures (Luo *et al.*, 2008). This implies that, when changes in pH occur in the environment, the available concentrations of arsenic in the LWAs will be greater than in the raw materials. Consequently, as in the case of Co, special care should be taken when the raw materials of LWAs show high As quantities. After the heating process, the reductions in the concentrations of Ba associated with F1, F2 and F3, in *W75S25-1225-15* with respect to *W75S25* mixture, and with F1 and F2, in *W50C50-1200-15* with respect to *W50C50* mixture, are very significant (Figs. 1e and 2e). Volatilization of Ba is not possible, due to the fact that this element's boiling point (1640ºC) is higher than the heating temperatures, as in the case of Be. Therefore, the above-mentioned geochemical forms of Ba must have changed to less bioavailable forms in the LWAs. They may have become associated with F4, in *W75S25-1225-15*, or with F3 and F4, in *W50C50-1200-15*, since the concentrations bound to these fractions increase ($ER_{Ba,F4}$=0.28, Fig. 1e; $ER_{Ba,F3}$=0.00 and $ER_{Ba,F4}$=0.61, Fig. 2e). In the case of the LWAs manufactured with *W* and *C*, other small proportions of the exchangeable, soluble and reducible Ba must have become a part of the undigested material obtained from the digestion of the LWAs, because the pseudo-total concentration decreases after the thermal treatment ($ER_{Ba,\copyright 1+2+3+4}$=2.08, Fig. 2e).

In *W75S25-1225-15*, Sr is the element with the highest concentration in the eluates obtained (0.75 mg/

kg, Table 4); in *W50C50-1200-15*, it is As (0.14 mg/kg, Table 4). It must be noted that all the studied elements are below the limit values for inert wastes in both types of LWAs. Finally, Table 5 shows an overview of the thermal effect on the leaching behaviour of the studied elements presenting the concentration trends in the non-residual fraction (the potential availability) and in the residual fraction. It is possible to establish two groups of elements from the standpoint of the thermal treatment effect:

i) Elements whose non-residual concentrations decrease after the thermal treatment: all the studied elements, except Ti, Mo and Sb. The elements in this group are more available in the raw materials than in the LWAs so the heating process is beneficial to the environment.

ii) Elements whose non-residual concentrations decrease or increase after the thermal treatment, depending on the mixture and/or type of LWAs: Ti, Mo and Sb.

CONCLUSION

Based on the obtained results in this study, it is possible to establish the following conclusions:

a. In the raw materials, the REEs are mainly associated with the reducible and residual fractions. The other studied elements are mainly associated with the residual fraction, with the exceptions of Mo, Ag, U, Sr, Ba, whose association depends on the studied raw material.

b. In the studied LWAs, all the studied elements are mainly associated with the residual fraction so their availability is relatively low.

c. Mn, in *W*, and Sr, in *C* and *SS*, are the elements which show the highest available concentrations when changes in pH occur, while Fe shows the highest available concentration when changes in the redox conditions of the three raw materials occur.

d. The thermal treatment reduces the availability of all the studied elements, with the exception of Ti, Mo and Sb, for which the availability depends on the studied LWA.

e. All the studied elements are in concentrations below the limit values for *inert wastes*.

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