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Chemical Speciation and Volatilization Evaluation of Heavy Metals Contained In Ceramic Blocks

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Abstract:- This work aimed to study the leaching characteristics of ceramic blocks produced with the incorporation of textile residues (15% w/w). For this, the procedures of sequential extraction and statistic analysis to validate the occurrence of metals volatilization during the burning process of the ceramic blocks were used. With a 95% confidence interval, the statistic analysis of the metals concentrations in the ceramic blocks, before and after the burning process, showed no metal volatilization. During the sequential extraction, Mn, Fe, Cr, Pb, Zn, Cu and Al distributions were observed mainly in their residual fractions of the textile residue solubilized/stabilized in the ceramic matrix. The sum of all involved fractions in the sequential extraction process is reasonably similar to the total content obtained after the digestion of the original samples with hydrofluoric acid and aqua regia. In both samples, ceramic blocks before and after the burning process, the percentages recoveries of 80 to 98% were achieved. This way, the solidification/stabilization process (S/S) showed to be efficient for the immobilization of heavy metals contained in textile residue (sludge) in ceramic blocks.

Keywords:- Clay, chemical speciation, textile residue, volatilization, solidification/stabilization process.

I. INTRODUCTION

The solidification/stabilization technique (S/S) is one of the ways of treatment and disposal of industrial residues. According to MALVIYA and CHAUDHARY [1] the solidification/stabilization (S/S) process utilizes chemically reactive formulations that, together with water and other sludge components, form stable solids. According to WENG et al. [2] the utilization of sludge as an addition to construction and building material, including ceramic blocks, not only converts the wastes into useful materials but it also alleviates the disposal problems. The prospective benefits of using sludge as the brick additive include immobilizing heavy metals in the fired matrix, oxidizing organic matter and destroying any pathogens during the firing process.

According to LI et al. [3], the study of the leaching behaviors of metals is an important way to obtain valuable information about the chemical speciation of contaminants in S/S matrix and their potential environmental risk. Leaching is the process by which contaminants are transferred from a stabilized matrix to liquid medium, such as water and other solutions.

Sequential extraction methods have often been used to study the speciation and the possible associations between metals and soil or sediments components [4,5]. The chemical partitioning of metals is operationally defined according to reagents used and matrix of the samples, which in the case of the present study is the clay. There may be some analytical limitations imposed by interference, selectivity and sensitivity of the sequential extraction methods, which could affect the differentiation of metals between various physicochemical forms in stabilized/solidified materials.

At present, a number of schemes have been proposed to fractionate metals basis of extractability of chemical reagents [6,7]. Of these methods, the sequential extraction method presented by TESSIER et al. [4] has been widely used in soil and sediment studies.

In the present work, ceramic blocks incorporated with textile waste (15% w/w) were analyzed according to the leaching characteristics of the solidification/stabilization (S/S) process by the sequential extraction method developed by TESSIER et al. [4]. Besides the chemical speciation, a statistical analysis of the metals concentrations presented in the ceramic blocks, before and after the burning process, was carried out with the objective of the evaluation of possible metal volatilization during the burning process of the ceramic blocks.

II. MATERIALS AND METHODS

a. Samples preparation

The residues (sludge) used in the experiments were obtained in fourteen textile industries from the region of Maringá-PR, Brazil. These residues were collected in the semi-dried state, mixed and homogenized in equal quantities, determined in percentage of dried mass. Clay from a local ceramic manufacturer was used as the solid matrix.

The clay and the dried residue were crushed in a bar-mill and screened to avoid the obstruction of the extruder by solid particles, what may compromise the blocks quality. Later on they were mixed, in percentage of dried mass, and homogenized.

Ceramic blocks with the proportion of 15% textile residue and 85% clay were produced in a laboratory extruder.

During the homogenization process the textile residue, sieved through a 2 mm mesh, were manually incorporated in clay mass. Later on, a bar mill with 30 Kg capacity of dried material was used. The dried textile residue/clay compound was sent to the ceramic manufacturer to finish the process of ceramic blocks fabrication.

In the local ceramic manufacturer, the textile residue/clay compound was introduced in the feed box of the mixer, humidified with water to facilitate the homogenization process, and then laminated in order to guarantee a better quality of the mixture process. The mixture in the form of a consistent layer was molded by extrusion, using Verdés equipment, with a production capacity of 80 blocks per min. and equipped with a vacuum chamber for removal of the incorporated air. The extruded mass was then introduced into an automatic unit with five tensioned steel wires for cutting the blocks in pre-defined sizes of 210 mm length. The produced blocks were, in the sequence, transported to drying sheds where they remained for seven days before the burning. The burning process was carried out in an industrial kiln for ceramic blocks for 72 hours, with temperatures ranging from 850 to 1000 º C. Later on, the burn blocks were cooled with forced ventilation during 12 h until they reached the ambient temperature. The ceramic blocks, before and after the burning process, were then collected for laboratory characterization.

The ceramic blocks were crushed and sieved through a 0,074 mm mesh and taken to an oven at 110 ^{o}C for 12 h before further laboratory analyses.

b. Analytical Methods

i. Total metals concentration

Total metal determinations were performed by hot acid digestion of the ceramic blocks, before and after the burning process. All analyses were performed in triplicates. About 0.2 g of sample was digested with 0.5 mL of aqua regia (HNO_3 and HCl in the proportion of 1:3 v/v) and 3 mL of hydrofluoric acid in Teflon flasks. The volume was significantly reduced until the sample solubilization. The system was then taken from the hot plat and cooled in water bath. After cooling, 10 mL of deionized water, 5 mL of 4% boric acid (H_3BO_3) and 1 mL of concentrated fuming Hydrochloric Acid (HCl) were added to the system, which was taken for additional heating until it reached a limpid aspect. Finally, it was cooled and transferred to a volumetric balloon of 100 mL which volume was completed with deionized water. The solution was stoked in a polyethylene flask.

A Varian SpectrAA 50B atomic absorption spectrophotometer was used for chemical elements determinations of the extracts from the acid digestion.

ii. Sequential Extraction

The sequential extraction Method used in this paper was the procedure developed by TESSIER et al. [4]. In this method the metals were operationally separated according to five fractions, defined as:

Fraction 1 – Changeable. The samples were extracted with 1.0 M $MgCl_2$ (pH 7.0) at a solid/solution ratio of 1:8, with continuous agitation at room temperature for 1 h.

Fraction 2 – Species bound in carbonate. The remaining solids from step (1) were extracted with 1 M NaOAc (adjusted to pH 5.0 with HOAc) at a solid/solution ratio of 1:8, with continuous agitation at room temperature for 5 h.

Fraction 3 – Species bound in Fe and Mn. The remaining solids from step (2) were extracted with 0.04 M NH2OH.HCl dissolved with HOAc 25% (v/v), at a solid/solution ratio of 1:20, with occasional agitation at 96 ± 3 ºC for 6 h.

Fraction 4 – Species bound in organic matter /sulfide. The remaining solids from step (3) were extracted with 0.02 M HNO_3 (at a solid/solution ratio of 1:3) and 30% H_2O_2 (adjusted to pH 2.0 with HNO_3), at a solid/solution ratio of 1:5, with occasional agitation at 85 ± 2 ºC for 2 h. A second aliquot of 30% H_2O_2 (adjusted to pH 2.0 with HNO_3), at a solid/solution ratio of 1:3, was added and the solution was heated at 85 ± 2 ºC for 3 h with sporadic agitation. After cooling, 3.2 M de NH_4OAc dissolved in 20% (v/v) HNO_3, was

added to the solution at a solid/solution ratio of 1:5 under continuous agitation. The solution was kept under these conditions for 30 min.
Fraction 5 – Residual. The remaining solids from step (4) were digested according to the procedure described in section 2.2.1 for total metals analyses.
Centrifugation was performed by 30 min between each successive extraction. Supernatant was carefully removed with a pipette for further analysis of trace metals.
All glassware used for the experiments was previously decontaminated with HNO_3 solution (20% v/v) and rinsed with distilled/deionized water prior to drying.
A Varian SpectrAA 50B atomic absorption spectrophotometer was also used for trace metals determinations (Mn, Fe, Cr, Pb, Zn, Cu and Al) of the extracts from each fractionation step.

c. Statistic Treatment

A significance test for the evaluation of the heavy metals volatilization during the burning process of the ceramic blocks with the incorporation of textile residues (15% w/w) was performed. This test evaluates the confidence limit between two averages, taken as a hypothesis that two sample data belong to the same universe [8].

The average is calculated to each sample data, $\bar{x}_1$ and $\bar{x}_2$, and each average is an estimate of an average of its universe, μ_1 and μ_2. It is entirely possible that $\bar{x}_1$ and $\bar{x}_2$ may differ, what means that $\bar{x}_1 - \bar{x}_2 = \Delta\bar{x} \neq 0$, simply due to the randomic dispersion of the data. This difference may occur even if two sample data were extracted from the same universe, what means, $\mu_1 = \mu_2$. Thus, $\Delta\bar{x}$ is an estimate of $\Delta\mu$. So, if the confidence limit for $\Delta\bar{x}$ if bigger than the own $|\Delta\bar{x}|$, there is a reasonable chance that $\Delta\bar{x}$ is zero and that $\Delta\mu = 0$.
Generally, the confidence limit for a data set is defined by:

$$\text{CL} = \pm t_{\alpha,\varphi} \cdot S_{dados}$$

Where, the data φ have degrees of freedom.
In this study, the interest remains in the confidence limit for $\Delta\bar{x}$, which is defined by:

$$\Delta\bar{x} = \bar{x}_1 - \bar{x}_2$$

The standard deviation for the data set is defined by:

$$S_{dados} = S_{\Delta\bar{x}} = S_x \cdot \left(\frac{1}{n_1} + \frac{1}{n_2}\right)^{1/2}$$

Where, n_1 and n_2 are the sample number in each data set and S_x is the standard deviation for the data as a whole. In this way, the equation of the Confidence limit may be re-written as:

$$\text{CL for } \Delta\bar{x} = \text{CL} = \pm t_{\alpha,\varphi} \cdot S_{\Delta\bar{x}} = \pm t_{\alpha,\varphi} \cdot S_x \cdot \left(\frac{1}{n_1} + \frac{1}{n_2}\right)^{1/2}$$

Where, $\varphi = n_1 + n_2 - 2$, once, in this case, two constants ($\bar{x}_1$ and $\bar{x}_2$) where calculated for the data.

III. RESULTS AND DISCUSSION

a. Total metals concentration and volatilization analyses

Table 1 presents the metal concentration in the ceramic blocks with an incorporation of 15% (w/w) of textile residue (sludge), before (BB) and after (AB) the burning process.

Table 1 - Total metals concentration (mg Kg^{-1}) in ceramic blocks before and after the burning process.

From the results presented in Table 1, it can be seen that there was an increase in the concentration of metals contained in the ceramic blocks after the burning process due to the organic matter and humidity volatilization.

In order to perform the significance test, a correction on the concentration of metals in the ceramic blocks with incorporation of 15% (w/w) of textile residue (sludge) after the burning process was made. Table 2 presents the concentration of metals in ceramic blocks after the burning process in a humid mass basis.

Table 2 - Total metals concentration (mg Kg^{-1}) in a humid mass basis in ceramic blocks after the burning process.

Table 3 presents the statistic treatment of the data (total metals concentration in the ceramic blocks before (BB) and after the burning (AB) process in a humid mass basis) by means of the significance test.

Table 3 - Significance test for the data set.

With an established confidence limit of 95%, it is possible to observe from Table 3 that there was no metals volatilization from the ceramic blocks during the burning process, since the situation CL > $\left|\Delta\bar{x}\right|$ was respected for all the cases.

The results confirm that the solidification/stabilization (S/S) process was capable of immobilizing the metals presented in the sludge in the ceramic blocks in an effective way. According to MALVIYA and CHAUDHARY [1] the solidification/stabilization (S/S) process uses chemically actives formulation, that with water and other sludge components, form stable solids.

b. Sequential Extraction

The results from the sequential extraction (Tessier Methods) carried out in ceramic blocks with an incorporation of 15% (w/w) of textile residue (sludge), before (BB) and after (AB) the burning process, and the percentage of metal recovery are listed in Table 4.

Table 4 - Results from each step of the sequential extraction of the ceramic blocks before (BB) and after (AB) the burning process.

Generally, the sum of all involved fractions in the sequential extraction process is reasonably similar to the total content obtained after the digestion of the original samples with hydrofluoric acid and aqua regia.

In both samples were reached recovery percentages between 80 to 98%. These values were similar to those mentioned in other bibliographic references [3,9,10].

According to USERO et al. [11] and HO [5], the principle of sequential chemical extraction methods is that various chemical extractants are applied successively to a sample, dissolving the components of the sample matrix in sequential order. Ideally, a reagent should liberate all the metals from a particular matrix's component (i.e. exchangeable, carbonate, etc.), and should not affect the metals in other components. However, it is generally recognized that the partitioning of metals obtained by such procedures is always operationally defined as it is affected by many experimental factors especially the chemical composition of the sample matrix.

Figures 1 and 2 show the metallic distributions for the ceramic blocks before and after the burning process, respectively.

Figure 1. Metallic distributions for the ceramic blocks before the burning process.

Figure 2. Metallic distributions for the ceramic blocks after the burning process.

The changeable fraction (fraction 1) corresponds to the metals that are directly extracted, once its extractive solution owns only a displacement power. With respect to the ceramic blocks after the burning process, from the obtained results, it is possible to observe that copper was the most solubilized metal in this sample. It can be explained by the fact that, after the burning process, the metals originally presented in the blocks before the burning process may have been associated to oxides and, due to the ionic radio difference, the formed metallic oxides own a greater capacity to self solubilize. The ionic radio for copper is 0.69 Å, while the ionic radio for oxygen is 1.40 Å. The inverse situation may be occurred to lead, which ionic radio is 1.20 Å, what means that this metal formed a stable binding with oxygen, resulting in a low solubility of this metal in the blocks after the burning process.

In the carbonate-bound fraction (fraction 2) an extractive solution that owned a slight acidity with the capability of decomposing the carbonates was used. In the ceramic blocks after the burning process there was an inversion in the solubilization results of lead and copper, and a slight inversion in the zinc solubilization. It may be due to the neutral oxides formed that reacted with these metals, resulting in a higher solubilization of these metals in the ceramic blocks after the burning process. Besides, as the extractive solution used in the methods is the same for both samples, it may be occurred, in this step, the solubilization of the metals not dissolved in the previous step.

A reducible fraction (Fe-Mn oxide bound fraction) constitutes the fraction 3. Lead and copper were solubilized in a higher proportion in the blocks after the burning process, indicating that these metals did not enter in the residual phase during the solidification/stabilization process.

The oxidizable fraction or bound in organic matter constitutes the fraction 4. Figures 1 and 2 show that manganese, lead, zinc and copper solubilized in a higher proportion in the sample of ceramic blocks after the burning process. The burning process of the ceramic blocks may be responsible for a binding of these metals to oxygen, which formed complex, is weaker. Besides, the use of hydrogen peroxide (H_2O_2) in the extractive solution may have favored the formation of complex oxygen-metals species. Thus, the standard potential of electrode (reduction) to the hydrogen peroxide, as well as to the complex of these metals possibly formed with oxygen according to SKOOG, WEST and HOOLER [12] is:

Reation	Eo, V^+	
$H_2O_2 + 2H^+ + 2e^- \rightleftarrows 2H_2O$	+ 1,776	(1)
$MnO_{2(s)} + 4H^+ + 2e^- \rightleftarrows Mn^{2+} + 2H_2O$	+ 1,230	(2)
$PbO_{2(s)} + 4H^+ + 2e^- \rightleftarrows Pb^{2+} + 2H_2O$	+ 1,455	(3)
$ZnO_2^{2-} + 4H^+ + 2e^- \rightleftarrows Zn_{(s)} + 2H_2O$	+ 0,441	(4)
$CuO + 2H^+ + e^- \rightleftarrows Cu^+ + H_2O$	+ 0,620	(5)

Fraction 5 is referred to the residual fraction. Regarding the ceramic block after the burning process (AB), all metals are mainly distributed in fraction 5, indicating that these metals were primarily fixed in the mineral structure of the ceramic block during the solidification/stabilization process.

This way, it is possible to observe that the chemical elements contained in the textile residues incorporated in the ceramic mass will remain immobilized in the ceramic material, without any environmental prejudice or risk for future generations caused by soil contamination during their life cycle. Thus, the solidification/stabilization (S/S) process was capable of immobilizing in an effective way the metals in the ceramic blocks.

IV. CONCLUSION

The integrated use of the sequential extraction procedure and statistic analysis of the total metal concentration of the ceramic blocks provides an efficient assessment of the leaching behavior of metals present in the textile solubilized/stabilized residue in the ceramic matrix.

Through statistical analysis of the total metals concentrations of the ceramic blocks it is possible to infer that there was no volatilization of them during the burning process of the ceramic blocks, proving the efficiency of the treatment employed in the textile residues.

During the sequential extraction procedure, the analyzed metals were distributed mainly in the residual fraction. Thus, the solidification/stabilization (S/E) process for the incorporation of the textile residues in the ceramic mass showed to be very efficient, stabilizing the heavy metals present in the textile residue in the ceramic matrix.

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Table 1 - Total metals concentration (mg Kg^{-1}) in ceramic blocks before and after the burning process.

Metal	ceramic blocks before the burning process -BB	ceramic blocks after the burning process - AB
Mn	894.2	**917.8**
	889.8	**909.6**
	901.7	**915.9**
average	**895.2**	**914.4**
Fe	32,588.5	**36,137.9**
	28,219.5	**34,046.9**
	34,730.4	**36,389.6**
average	**31,846.2**	**35,524.8**
Cr	89.1	**103.0**
	88.7	**103.3**
	87.7	**102.1**
average	**88.5**	**102.8**
Pb	69.2	**77.5**
	67.7	**76.3**
	66.6	**77.6**
average	**67.8**	**77.1**
Zn	181.8	**202.3**
	177.2	**201.4**
	177.6	**203.4**
average	**178.6**	**202.4**
Cu	79.3	**96.9**
	84.4	**99.4**
	82.3	**93.4**
average	**82.0**	**96.5**
Al	66,524.9	**74,037.5**

	68,145.9	**76,294.1**
	67,129.8	**74,592.2**
average	**67,266.9**	**74,974.9**
Na	11,298.1	**15,596.5**
	11,139.7	**15,933.7**
	12,163.8	**16,426.9**
average	**11,533.8**	**15,985.6**

Table 2 - Total metals concentration (mg Kg^{-1}) in a humid mass basis in ceramic blocks after the burning process.

Metal	Sample	ceramic blocks after the burning process - AB
Mn	**AB_1**	**755.4**
	AB_2	**748.7**
	AB_3	**753.9**
Fe	**AB_1**	**29,744.0**
	AB_2	**28,023.0**
	AB_3	**39,951.2**
Cr	**AB_1**	**84.8**
	AB_2	**85.0**
	AB_3	**84.0**
Pb	**AB_1**	**63.8**
	AB_2	**62.8**
	AB_3	**63.9**
Zn	**AB_1**	**166.5**
	AB_2	**165.8**
	AB_3	**167.4**
Cu	**AB_1**	**79.7**
	AB_2	**81.8**
	AB_3	**76.8**
Al	**AB_1**	**60,938.1**
	AB_2	**62,795.4**
	AB_3	**61,394.7**
Na	**AB_1**	**12,837.0**
	AB_2	**13,114.5**
	AB_3	**13,520.5**

Table 3 - Significance test for the data set.

Metal	Sample	Concentration (mg kg^{-1})	$\bar{x}$	$\lvert\Delta\bar{x}\rvert$	CL	Status
Mn	AB_1	755.4	752.6	135.7	168.8	**No volatilization**
	AB_2	748.7				
	AB_3	753.9				
	BB_1	894.2	895.2			
	BB_2	889.8				
	BB_3	901.7				
Fe	AB_1	29,744.0	29,239.4	4.8	11.6	**No volatilization**
	AB_2	28,023.0				
	AB_3	39,951.2				
	BB_1	32,588.5	31,846.1			
	BB_2	28,219.5				

	BB_3	34,730.4				
Cr	AB_1	84.8	84.6	3.1	4.1	**No volatilization**
	AB_2	85.0				
	AB_3	84.0				
	BB_1	89.1	88.5			
	BB_2	88.7				
	BB_3	87.7				
Pb	AB_1	63.8	63.5	3.8	5.1	**No volatilization**
	AB_2	62.8				
	AB_3	63.9				
	BB_1	69.2	67.8			
	BB_2	67.7				
	BB_3	66.6				
Zn	AB_1	166.5	166.6	10.8	13.9	**No volatilization**
	AB_2	165.8				
	AB_3	167.4				
	BB_1	181.8	178.9			
	BB_2	177.2				
	BB_3	177.6				
Cu	AB_1	79.7	79.5	1.8	5.6	**No volatilization**
	AB_2	81.8				
	AB_3	76.8				
	BB_1	79.3	82.0			
	BB_2	84.4				
	BB_3	82.3				
Al	AB_1	60,938.1	61,709.4	4,995.8	6,465.7	**No volatilization**
	AB_2	62,795.4				
	AB_3	61,394.7				
	BB_1	66,524.9	67,266.9			
	BB_2	68,145.9				
	BB_3	67,129.8				
Na	AB_1	12,837.0	13,157.3	1,743.2	2,357.0	**No volatilization**
	AB_2	13,114.5				
	AB_3	13,520.5				
	BB_1	11,298.1	11,533.8			
	BB_2	11,139.7				
	BB_3	**12,163.8**				

Table 4 Results from each step of the sequential extraction of the ceramic blocks before (BB) and after (AB) the burning process.

Metal	Step	BB		% Recovery	AB		% Recovery
		mg Kg^{-1}	%		Mg Kg^{-1}	%	
Mn	1	110.1	12.3	92.6	60.7	6.6	**81.8**
	2	199.2	22.3		36.8	4.0	
	3	147.3	16.5		89.7	9.8	
	4	30.5	3.4		66.1	7.2	
	5	341.8	38.2		495.0	54.1	
average $_{\text{sample digestion}}$ (mg Kg^{-1})		895.2			914.4		
Fe	1	0.8	0.0	91.0	1.4	0.004	**80.3**
	2	108.0	0.3		43.5	0.1	
	3	1,594.9	5.0		429.2	1.2	
	4	98.2	0.3		30.2	0.1	
	5	27,179.3	85.3		28,023.0	78.9	
average $_{\text{sample digestion}}$		31,846.2			35,524.8		

(mg Kg^{-1})							
Cr	1	5.8	6.5	93.5	5.9	5.7	**82.4**
	2	3.8	4.3		2.8	2.7	
	3	12.0	13.6		11.5	11.2	
	4	2.5	2.8		0.8	0.7	
	5	58.6	66.2		63.9	62.1	
average $_{\text{sample digestion}}$ (mg Kg^{-1})		88.5			102.8		
Pb	1	0.6	0.9	94.3	0.5	0.7	**85.2**
	2	1.4	2.1		3.8	4.9	
	3	7.3	10.8		24.0	31.1	
	4	0.5	0.7		3.3	4.2	
	5	54.2	79.8		34.2	44.3	
average $_{\text{sample digestion}}$ (mg Kg^{-1})		67.8			77.1		
Zn	1	4.7	2.6	97.2	0.5	0.2	**88.4**
	2	18.4	10.3		25.6	12.6	
	3	36.2	20.3		32.0	15.8	
	4	8.9	5.0		18.5	9.1	
	5	105.6	59.1		102.3	50.5	
average $_{\text{sample digestion}}$ (mg Kg^{-1})		178.9			202.4		
Cu	1	0.1	0.1	91.7	2.6	2.7	**81.6**
	2	5.2	6.3		18.8	19.5	
	3	5.7	7.0		9.2	9.5	
	4	-	-		2.1	2.2	
	5	64.2	78.3		46.1	47.7	
average $_{\text{sample digestion}}$ (mg Kg^{-1})		82.0			96.5		
Al	1	-	-	89.6	-	-	**82.1**
	2	1,283.2	1.9		65.6	0.1	
	3	2,959.8	4.4		2,785.2	3.7	
	4	1,223.6	1.8		271.7	0.4	
	5	54,834.4	81.5		58,457.4	78.0	
average $_{\text{sample digestion}}$ (mg Kg^{-1})		**67,266.9**			**74,974.6**		

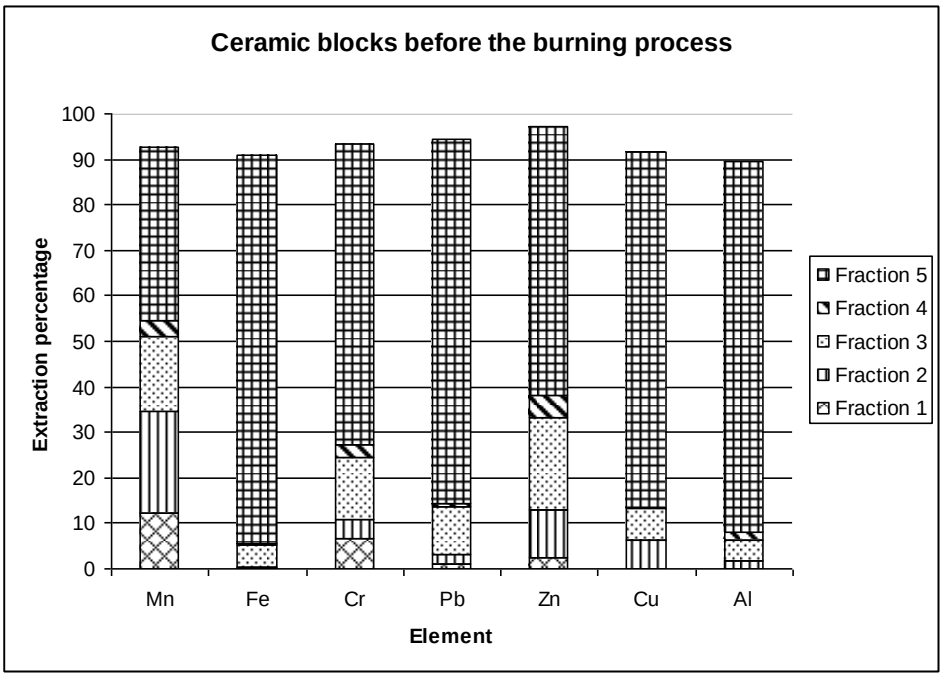

Figure 1. Metallic distributions for the ceramic blocks before the burning process.

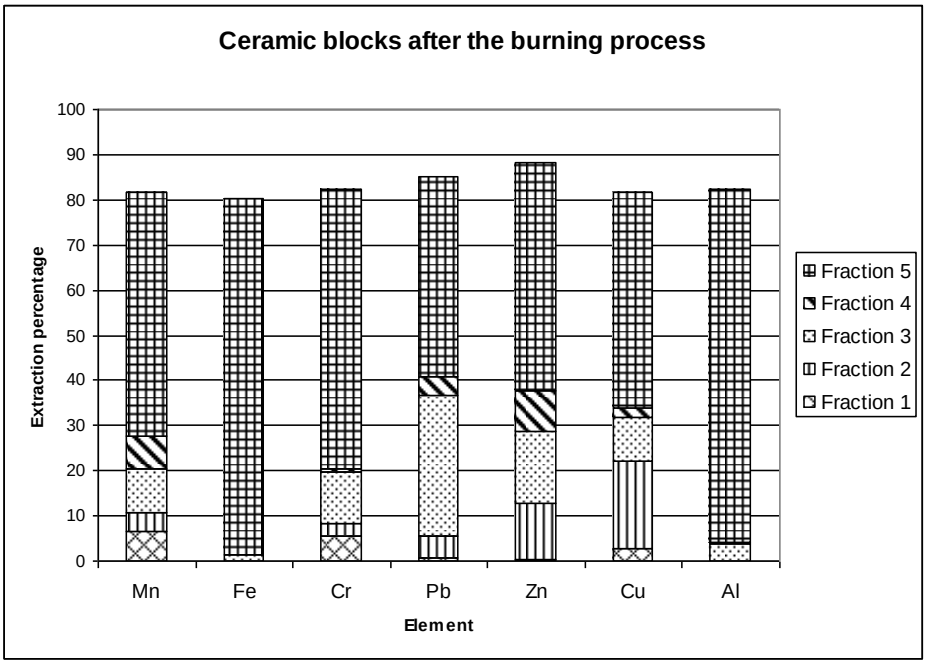

Figure 2. Metallic distributions for the ceramic blocks after the burning process.