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LEACHABILITY OF HEAVY METALS FROM SLAG RESIDUES UNDER INTENSE TEMPERATURE AND STIRRING CONDITIONS

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Abstract

Air cooled and water cooled slag samples were obtained from a demonstration plasma gasification / vitrification unit. The leachability of the major heavy metals present (Cr, Cu, Mn, Fe, Pb and Zn) in both the air cooled and water cooled slag when in contact with acidic solutions was investigated under different temperature, stirring and contact time conditions. Water cooled slag showed better resistance to heavy metals leaching. The vitrification process immobilised Cr and Pb. The leachability of Cu, Fe and Zn increased by heating and stirring, whereas the leachability of Mn was not affected by temperature and it was found to decrease with combined heating and stirring.

Keywords: gasification - vitrification unit, metal leachability, slag, stirring, temperature

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1. Introduction

According to the New Waste Framework Directive 2008/98/EC, the waste treatment methods are categorized as “Disposal” or “Recovery” and the thermal management practices that are accompanied by significant energy recovery are included in the “Recovery” category. In addition, the pyramid of the priorities in the waste management sector shows that energy recovery is more desired option in relation to the final disposal.

Gasification can be used as Waste-to-Energy process. In the case of plasma gasification, electricity is fed to a torch. The torch has two electrodes that create an arc, through which the process gas passes and is heated to internal temperatures that can reach 10,000°C (Gomez et al., 2009; Juniper, 2006; Mollah et al., 2000). Fig. 1 illustrates how the plasma torch operates.

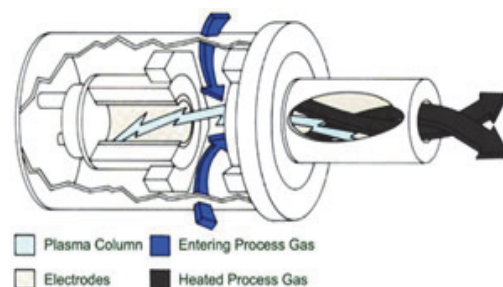


Fig. 1. Illustration of the operation of a plasma torch (Westinghouse)

The high temperatures result in achieving complete conversion of carbon-based materials to syngas composed primarily of H₂ and CO, while the inorganic materials are converted to a solid, vitreous slag (Kazemi and Macoveanu, 2012). The syngas can be utilized in boilers, gas turbines, or internal

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combustion engines to generate electricity, while the slag is inert and can be used as gravel.

The Unit of Environmental Science & Technology of the National Technical University of Athens attempted for first time to apply a gasification process in Greece (Moustakas et al., 2005). The plasma generator in the unit used is located within the waste treatment reactor. The unit that had initially been installed in the Viotia Region for the treatment of hazardous waste (Moustakas et al., 2008) was then modified in order to be used for the treatment of different types of waste including municipal waste, too. A general view of the whole demonstration facility is provided (Fig. 2).



Fig. 2. General view of the gasification / vitrification unit

Apart from air emissions that constitute the main environmental concern when applying thermal techniques for waste treatment, attention should also be drawn to the produced solid residues and the potential adverse effects during their use or disposal, especially with respect to heavy metals leaching. The solid residue of the gasification / vitrification process that is called slag was poured out periodically from the furnace. Two methods were used to cool slag.

The first method used air as the cooling means, with the slag to be poured into a slag mold to form ingots (air-cooled slag, designated as ACS, Fig. 3), whereas the second method used water with the slag to be quenched in a water tank forming granulated slag (water cooled slag, designated as WCS, Fig. 4).



Fig. 3. Air cooled slag



Fig. 4. Water cooled slag

The first is characterized as a bulky and compact material, while the second is obtained in granular form (Moustakas and Loizidou, 2010).

The objective of this work was to determine the influence of temperature, stirring and contact time to the leaching properties of both ACS and WCS generated by gasification/ vitrification unit (Moustakas et al., 2005, 2008). The leaching behaviour of the metals contained in slags is a subject of scientific interest that is currently being investigated (Gheorghe et al., 2009; Guo et al., 2013; Kuo et al., 2008a, 2008b; Saffarzadeh et al., 2006, 2009; Wei et al., 2014).

Previous leaching experiments using slag samples led to the essential conclusion that both ACS and WCS produced are comprised mostly of amorphous glassy phases. The findings of the experiments indicated that the vitrified slag is stable and inert and that it can be disposed safely meeting the requirements that the Toxicity Characteristic Leaching Procedure (TCLP) and the Decision 2003/33/EC set. Furthermore, pH, particle size and cooling method were found to affect the leaching behavior of slag. With regard to the latter parameter, it was identified that when rapid cooling takes place, stabilization of metals in the glass phase is improved and acid resistance of the slag is increased. Experiments on the leachability of Cu, Mn, Fe, Zn, Pb and Cr from slag samples indicated that Cr and Pb were immobilized by the vitrification process, whilst the leaching amounts of Cu, Mn, Fe and Zn were rather high at low pH values. Furthermore, the samples with smaller particles lead to higher metal leaching concentrations than those of larger particles (Moustakas et al., 2012).

2. Experimental design

After pH and particle size, temperature and stirring were identified as critical parameters to be studied to determine their influence in the leaching behavior of ACS and WCS. To examine the effect that intense conditions have on the metal leachability of slag, samples with a specified small particle size were put in contact with water solutions of specified low pH value under different temperature and stirring conditions.

2.1. Measurement of the heavy metal content in ACS and WCS

Both ACS and WCS samples were digested in with acids so as to assess the metal content of the produced slag. 0.5 g of each of the samples were digested in acids using a special digestion device (HACG/23120-21,-21). The US EPA Method 3051, Microwave assisted acid digestion of sediments, sludges, soils, and oils was used. After 5 minutes under the temperature of 440°C, 16.7 mL of H₂O₂ were added in the bottles and the procedure was stopped within a minute after the last drop had fell. Before being filtered under vacuum conditions, the conical bottles were left to cool. Atomic Absorption Spectrometry (AAS) (Fast Sequential Atomic Absorption Spectrometer VARIAN AA24OFS) was used to determine the metal content of the samples. The Standard Method Number used for the metal content determination was: US EPA 3051A:2007 / APHA-AWWA-WEF Standard Methods: 3111, 2012 / ISO 11465:1993. The formula used to calculate the contained metals in the slag is provided below (Eq. 1):

$$C_{in} = C_m^* (V_m / 1000) / (1000 / 0.05) \quad (1)$$

where: *C_{in}*: the concentration of metal within the slag sample; *C_m*: the concentration of metal in the solution (measured by AAS); *V_m*: volume of filtrate solution (Tan, 1996).

2.2. Evaluation of the leaching properties under different stirring and temperature conditions

Batch experiments were conducted to assess the leachability of heavy metals from ACS and WCS, with fine grained particles with diameter less than 150µm (d<150µm) to have been put in contact with an acidic solution of pH 4. It is highlighted that both pH conditions and particles size were selected to guarantee conditions favoring leaching. Fine grained slag particles were selected as more appropriate for the experiments because of their larger surface area in contact with the solution, a factor that guarantees increased leachability. In addition, the high acidic conditions of pH equal to 4 were selected not only to ensure increased leachability, but also to simulate conditions that are possible to be met in a natural environment at extreme conditions. To conduct the experiments, both slag samples were powdered and sifted (using a hammer, a mortar and a suitable sieve) so as to receive the fine-grained particles fraction with diameter less than 150 µm (d<150µm). The samples were dispersed using deionized water with a ratio of

solid (kg) to liquid (l) equal to 1/20. The experiments were conducted for both ACS and WCS, with samples of 2 g to be added in 40 mL of deionized water and the pH was adjusted to 4. Solution of concentrated sulphuric acid was used to produce the solutions of pH 4. The original solution was diluted using deionized water until reaching the desired pH value.

The ACS samples were left under three different conditions:

- room temperature conditions (25°C),
 - high temperature conditions (45°C) and
 - room temperature and stirring conditions (25°C and 300 rounds / min),
- while the WCS samples were left under:
- room temperature conditions (25°C),
 - high temperature conditions (45°C) and
 - high temperature and stirring conditions (45°C and 300 rounds / min)
- for different time intervals (7 days, 20 days, 44 days, 54 days and 64 days).

3. Results and discussion

3.1. Heavy metal content in slag

Table 1 presents the heavy metal content in slag samples obtained by acid digestion of samples. The results indicate that the slag samples contained six different metals. Except for the content of Zn, WCS presented a bit higher metal content compared to ACS. Both ACS and WCS presented high contents of Fe and Mn. Neither Ni (detection limit: 0.77mg/kg) nor Cd (detection limit: 0.07mg/kg) was detected in the slag samples used.

3.2. Evaluation of the leachability of heavy metals under different temperature and stirring conditions

According to the outcomes of the experiments only some of the metals contained in the samples were extracted at detectable level. In all cases concentrations of Pb and Cr were not detectable in the leachate obtained. Figs. 5 a-d present the results of the leaching experiments for ACS samples. Fig. 5a shows the Cu leachability from ACS under the three different conditions, the temperature is the only factor that increased Cu leaching substantially. More specifically, the increase of the temperature from 25°C to 45°C increased the maximum Cu leaching percentage by 4 times (from about 4% to 16%). Furthermore, it should be noted that at 25°C the Cu concentration in the leachate is stabilized much earlier than in the case of the higher temperature, where the relevant stabilization takes place after 54 days.

Table 1. The metal concentration in WCS and ACS

Sample	Concentration of the metals measured in WCS and ACS after digestion (mg/kg)							
	Cr	Cu	Mn	Fe	Ni	Cd	Pb	Zn
WCS	27.7	118.7	264.9	1,188.2	Not detected	Not detected	47.4	147.4
ACS	25.9	32.2	133.6	715.9	Not detected	Not detected	38.9	160.4

The application of stirring also increases the leaching of Cu, but at a lesser extent than the temperature increase. The maximum Cu leached when stirring was applied and is closer to the percentage of Cu leached at room temperature (25°C) conditions. Furthermore, the contact time required for the stabilization of the Cu concentration in the leachate in the case stirring conditions is similar to that required at room conditions.

Fig. 5b presents the results for Mn. Heating and stirring conditions contributed very little to the leachability of Mn. In all the different conditions used, both Mn leaching and the relevant contact time required for the stabilization of the Mn concentration did not differ much. The maximum of 45% of Mn was leached at room conditions, totally opposite to the results obtained for all the other metals under study. Moreover, it can be observed that the increased degree of Mn leaching is evident for the first twenty days and then the stabilization process gradually takes place.

The Fe leaching percentage is shown in Fig. 5c. In the case of Cu leaching, temperature was found to be the influencing factor, while in the case of Fe, it was the stirring. When stirring is applied, no further increase of Fe leaching is noted after 44 days and the maximum content of Fe leached is almost four times greater than that at room temperature conditions and around two times higher than the percentage extracted at 45°C.

It is concluded that the influence of the heating and stirring in the Zn leachability is limited (Fig. 5d).

The maximum percentage of Zn amount (approximately 25%) is similar under all conditions investigated and it was reached after 64 days. Slightly higher leaching percentages are obtained under stirring conditions, followed by leaching percentages at high temperature and then at room temperature conditions. The results of the experimental series regarding the WCS samples are presented in Fig. 6.

Cu leaching behaviour under room temperature conditions, high temperature conditions and high temperature and stirring conditions is shown in Fig. 6a. As expected, the combination of stirring and heating results in the higher Cu extraction from the slag. The difference of the maximum Cu leaching percentage under high temperature conditions and at room temperature conditions without stirring is not efficient. Compared with the results in Fig. 5a, it may be concluded that the role of temperature towards the increase in Cu leaching is more obvious in the case of ACS. Moreover, Cu leaching is realized more slowly under room conditions during the first 20 days.

Fig. 6b summarizes the results for Mn. Like in the case of the ACS samples, Mn leaching is also favourable under room temperature conditions. No increase is noted in the Mn leaching percentage after 44 days. It is noteworthy that the highest Mn leaching was obtained under room temperature conditions: heating induced only half of the concentration obtained at room temperature, while heating and stirring combined had almost no effect on Mn leaching.

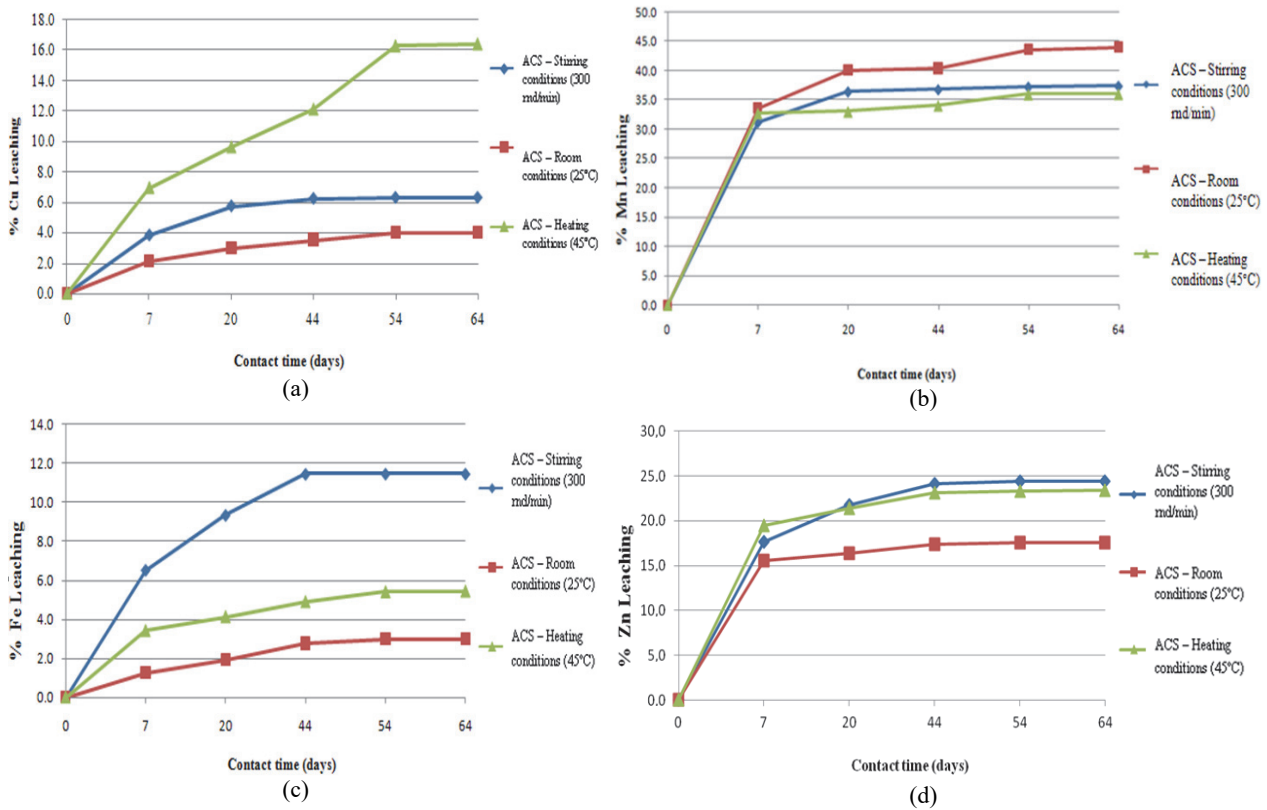


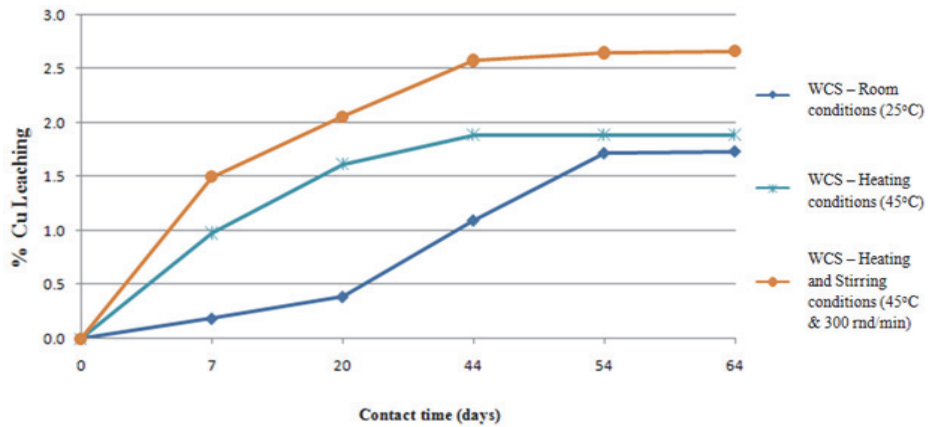
Fig. 5. Percentage of metal extraction from ACS under different conditions in dependence of time: (a) Cu leachability from ACS, (b) Mn leachability from ACS, (c) Fe leachability from ACS, (d) Zn leachability from ACS

In Fig. 6c experimental data regarding the Fe leaching percentage are presented. The leaching experiment under heating and stirring conditions presents the highest values of Fe leaching, but not differing much from those measured at high temperature conditions without stirring.

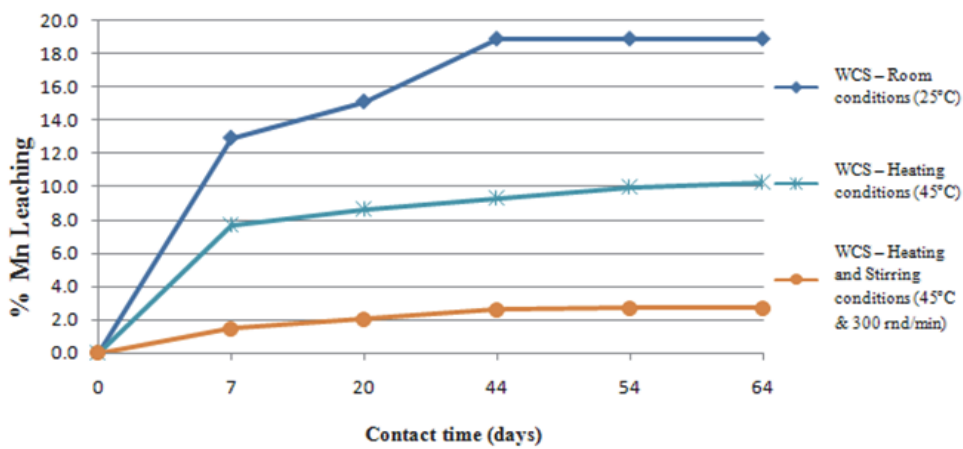
The results concerning Zn are given in Fig. 6d. As in the case of ACS samples, the maximum Zn leaching percentage at 45°C is similar, only slightly higher, to the percentage extracted at 25°C. Nevertheless, the combination of both heating and stirring conditions is followed by a considerable increase of Zn leaching, six times more than that under

room temperature conditions. The comparison of the experimental results concerning metal leachability from ACS and WCS and presented in Fig. 5 and Fig. 6 respectively show that metal leaching is enhanced in ACS samples.

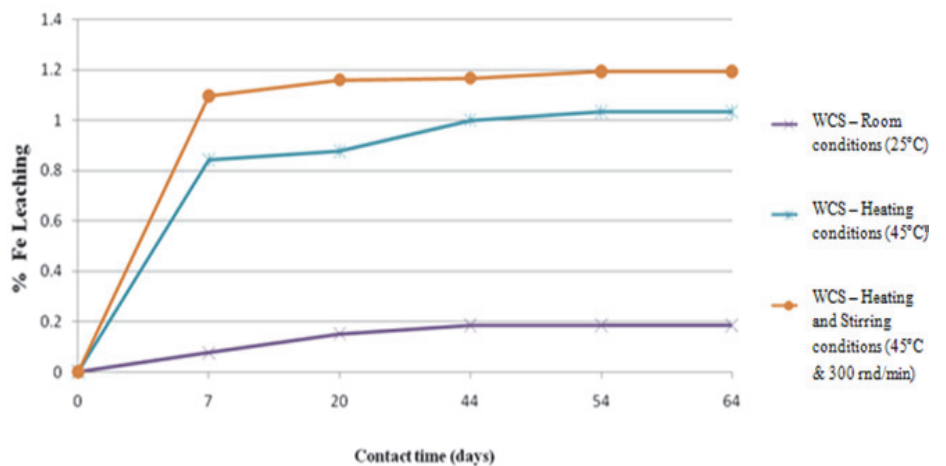
Water quenching can enhance a more uniform distribution of the glassy amorphous phase. The figures referring to the role of the cooling method, as well as the stirring and temperature conditions in the maximum metal leaching percentages in the case of the slag samples with a diameter of particle size lower than 150 µm at pH value 4 are given below (Figs. 7a-d).



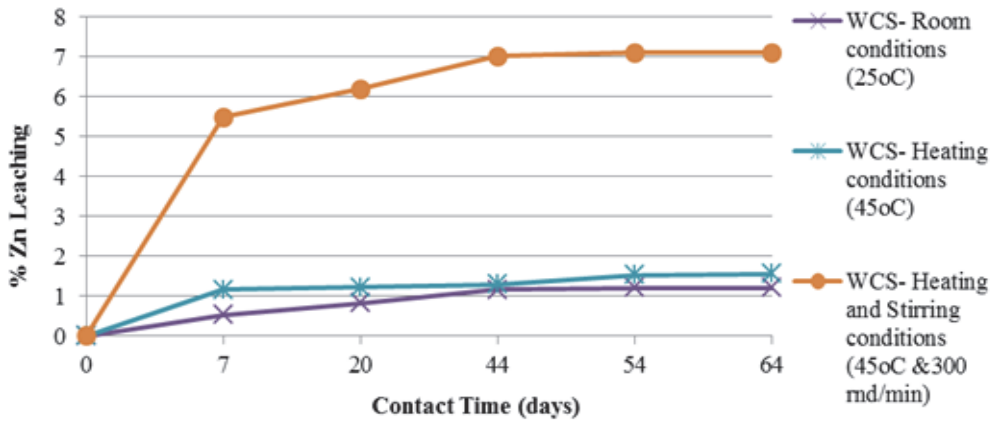
(a)



(b)

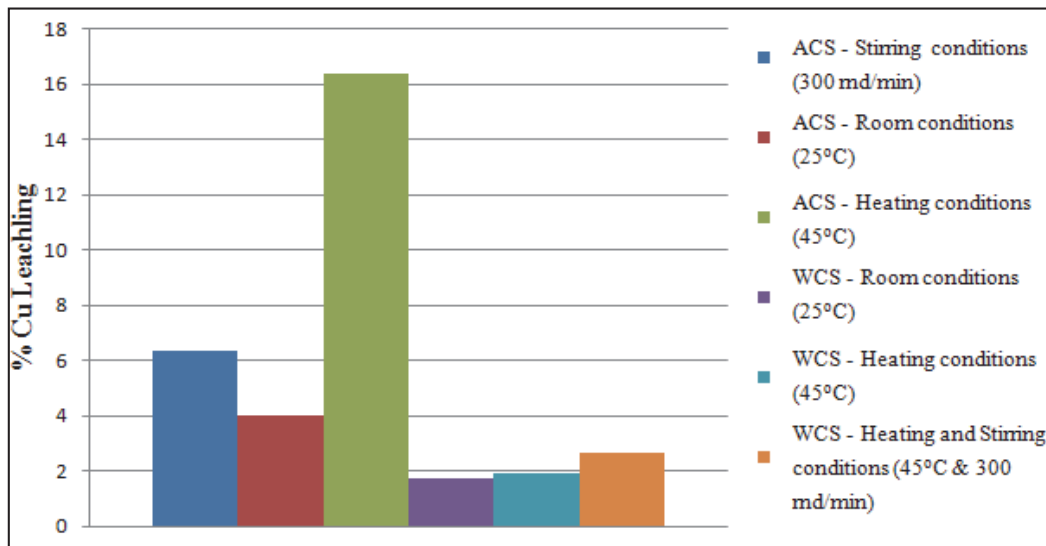


(c)

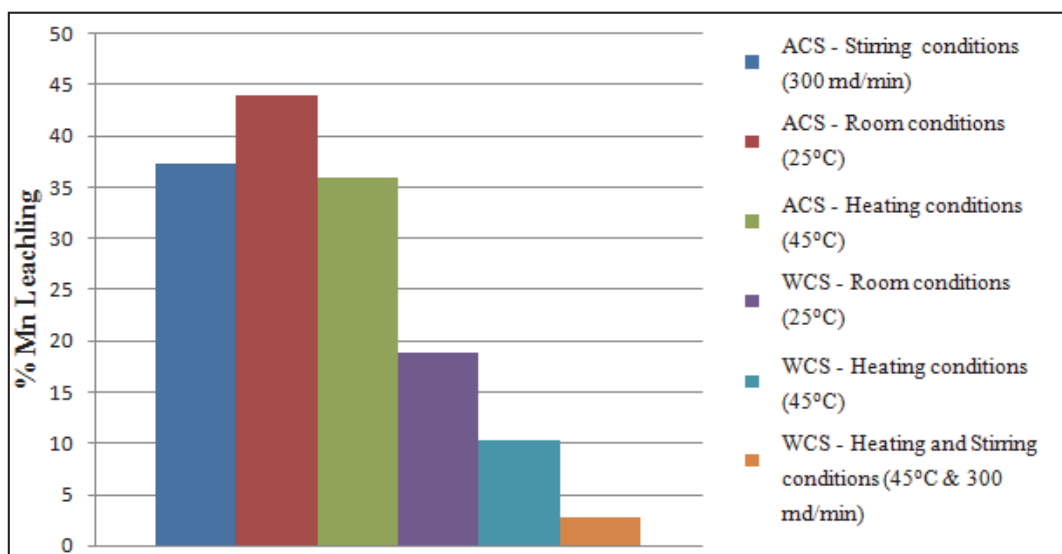


(d)

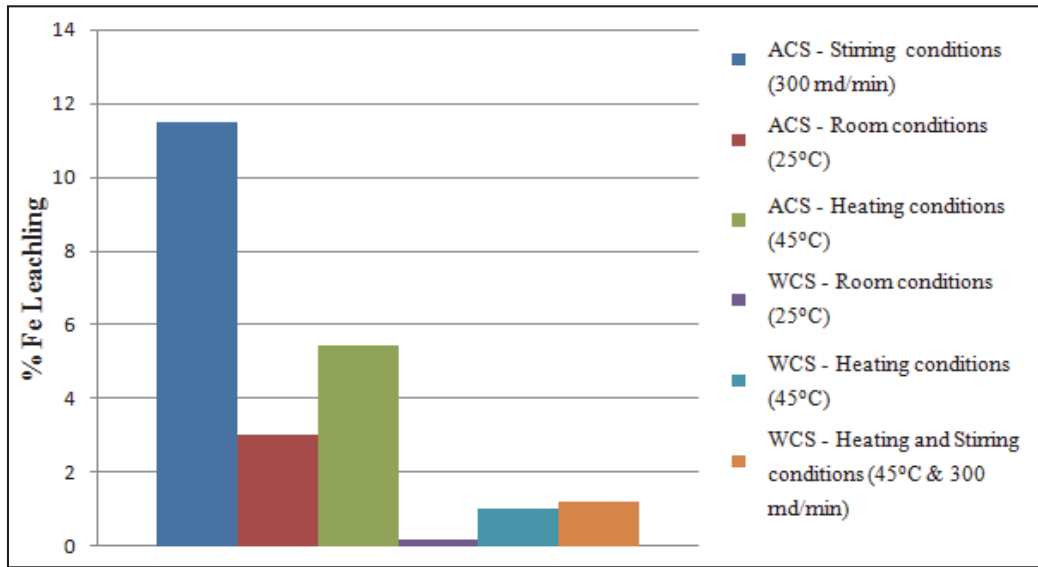
Fig. 6. Percentage of metal extraction from WCS under different conditions in dependence of time: (a) Cu leachability from WCS, (b) Mn leachability from WCS, (c) Fe leachability from WCS, (d) Zn leachability from WCS



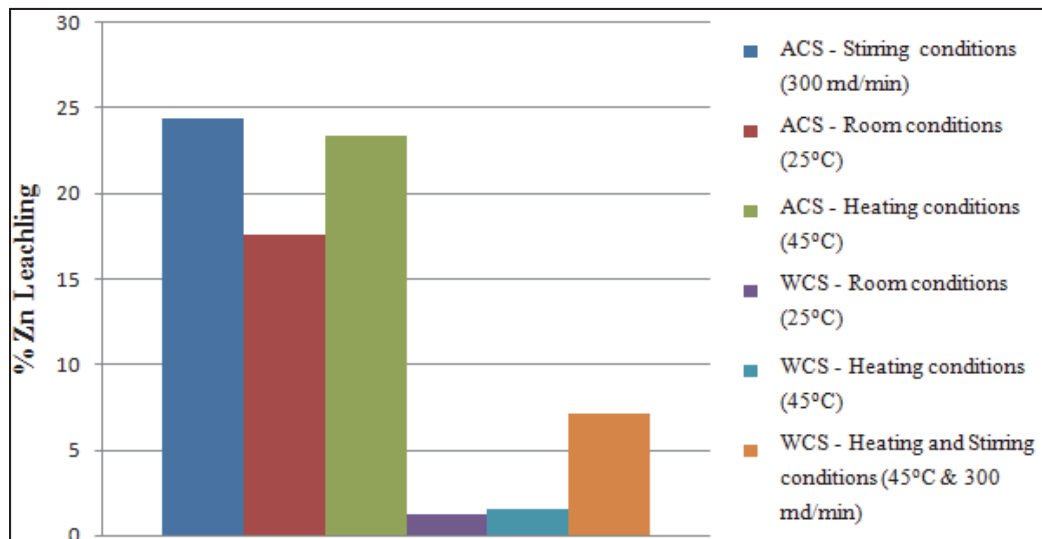
(a)



(b)



(c)



(d)

Fig. 7. The comparison of maximum metal leaching under different conditions: (a) % Cu leaching, (b) % Mn leaching, (c) % Fe leaching, (d) % Zn leaching

Fig. 7a refers to the results of Cu. The high temperature conditions in the case of ACS samples can cause the maximum metal extraction. In all cases, Cu extraction from WCS is less than extraction from ACS. The influence of the different stirring and temperature conditions for WCS is very limited.

Fig. 7b summarizes the maximum Mn leaching percentages. The application of either heating or stirring reduces the percentage of Mn extracted, while the combination of both heating and stirrings seems to limit Mn leaching even more. Therefore, compared to the leaching behavior of all the other metals under investigation, Mn exhibits a unique behavior. WCS samples were also found more resistant to Mn leaching, but this constitutes common conclusion for all metals examined. Fig. 7c refers to the results of Fe. Stirring conditions seem to play a crucial role in the

case of ACS, and they proved to be rather unimportant on the case of WCS. Fig. 7d refers to the data of Zn. The role of stirring and heating seems negligible in the case of ACS samples. Regarding WCS, the combination of high temperature and stirring seems to increase the leaching degree substantially, while heating alone does not really affect the maximum Zn leaching percentage significantly.

4. Conclusions

The use of water instead of air as cooling means for the produced slag can decrease metal leachability. Cr and Pb were fully immobilized by the vitrification process. The study of the leaching properties of Cu, Mn, Fe and Zn under different temperature and stirring conditions proved that high

temperature and stirring generally lead to increase of metal extraction for Cu, Fe and Zn, while the opposite was observed in the case of Mn, where the maximum leaching values were noted in room temperature conditions.

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