

REDUCTION OF P LEVELS IN THE LEATHER INCINERATION ASHES FOR THE PRODUCTION OF FeCr FERROALLOY¹

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Abstract

The aim of this study is the evaluation and determination of a hydrometallurgical route for the best cost / benefit for the reduction of P content in the ash from the leather shavings incineration (ALSI). The ash, with high Cr content, serve as raw material for the production of Fe-Cr alloys. Some batches, however, have high levels of P – element that is harmful to the steels properties. Routes based on acid dissolution of P compounds contained in the ALSI were evaluated in laboratory level. Aqueous solutions of acids HCl and H₂SO₄ were compared and the decision favored the use of HCl. Using the FactSage 6.2 application, simulations were performed to verify the action of HCl on P in ALSI. The method chosen, however, is characterized by the *in situ* production of HCl by mixing solutions of H₂SO₄ and NaCl – this fact enhances the removal of the P in ALSI. Moreover, both the NaCl and H₂SO₄ are low cost products, which allows reuse of Cr contained in ALSI of higher P levels.

Key words: Incineration; Recycling; Leather waste; Leaching.

REDUÇÃO DOS TEORES DE P EM CINZAS DA INCINERAÇÃO DE COURO PARA A PRODUÇÃO DE FERROLIGA Fe-Cr

Resumo

O objetivo desse trabalho consiste na avaliação e determinação de uma rota hidrometalúrgica de melhor custo/benefício para a redução do teor de P nas cinzas da incineração de resíduos de couro (CIAC). As cinzas, pelo elevado teor de Cr, servem de matéria-prima para a obtenção de ligas Fe-Cr. Algumas bateladas, contudo, possuem alto teor de P – elemento que é prejudicial às propriedades dos aços. Foram avaliadas, em nível de laboratório, rotas baseadas na dissolução ácida dos compostos de P contidos na CIAC. Foram comparadas soluções aquosas dos ácidos HCl, H₂SO₄ e se optou pelo HCl. Com o uso do aplicativo FactSage 6.2 foram feitas simulações para verificar a ação do HCl sobre o P da CIAC. O método escolhido, contudo, caracteriza-se pela produção *in situ* de HCl pela mistura de soluções de H₂SO₄ e NaCl – fato que potencializa cineticamente a remoção do P da CIAC. Além disso, tanto o H₂SO₄ quanto o NaCl são produtos de baixo custo, que viabilizam a reutilização do Cr contido na CIAC contendo alto nível de P.

Palavras-chave: Incineração; Reciclagem; Resíduos de couro; Lixiviação.

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1 INTRODUCTION

1.1 Chromium-Containing Wastes

In the leather tanning industry, raw skin, or hide, is transformed into leather by means of a series of chemical and mechanical operations. Chromium salts (in particular chromium sulphate) give leather several good properties and are therefore the most widely used tanning substances today.

Activities related to leather tanning and leather goods processing, however, have a high impact on the environment due to the great quantity of process residues. The effluents and pollutants – generated from different sources during the multi-step operations – are classified as dangerous by the Brazilian Legislation, mainly due to the presence of chromium. The landfilling of these residues is of great concern; nevertheless, simple stockpiling is no solution and the accumulated amount of waste has steadily increased during the past years.

One alternative to sanitary landfill is given by the thermal treatment which involves incineration, gasification, and pyrolysis as means of treatment. Next to energy recovery from waste, the volume reduction attained by this type of treatment – ca. 90% – is very significant.⁽¹⁾

1.2 Incineration Ashes

This practice of incineration generates *ashes from leather shavings incineration*, hereinafter referred to as ALSI.

Providentially, ALSI act as a receptacle for the metal chromium contained in leather. This makes the ALSI rich in chromium oxide (up to 50%-60% Cr₂O₃). On the other hand, – despite the reduction in volume – because of the presence of chromium, the deposition of the material is not advised.

The Cr contained in the ALSI was already object of research that focused in its reuse. The material has been considered e.g. for the production of refractory materials,⁽²⁾ in ceramics⁽³⁾ and for the production of tanant chemicals (chromium sulphate).⁽⁴⁻⁶⁾

Due to the high concentration of chromium oxide in ALSI, this material could be used as a *chromite* (FeO·Cr₂O₃) substitute in the production of ferrochrome alloy by carbothermic reduction.

However, compared with chromite, ALSI has a very high content of phosphorus – originated from the chemicals used in the hide processing step⁽⁷⁾ (Table 1).

Table 1. Cr and P content (given as oxides) [wt.-%] in ALSI; the high degree of heterogeneity is reflected in the given figures

Oxide	Wenzel ⁽⁸⁾	Godinho ⁽⁹⁾	Pereira ⁽⁴⁾	Padilha ⁽⁷⁾
Cr ₂ O ₃	62.29	55.91	55.01	55 ± 4
P ₂ O ₅	2.58	1.59	0.95	3.26 ± 0.30

Phosphorus is an undesirable element in steel. When present in stainless steel, is tolerated only in very low quantities (P < 0.035%). Detrimental effects of phosphorus in steel include various forms of embrittlement which reduce the toughness and ductility.

Within this context, this research aims to study methods of dephosphorization of ashes derived from incineration of leather waste, by means of acid leaching. Thus, it

will be perfectly feasible to use the chromium contained in the leather shaving ashes in the production of stainless steel even when this material shows a high level of phosphorus. The production of a High Carbon FeCr alloy (HC-FeCr) with ashes from leather shavings incineration (ALSI) was already investigated theoretically and at the laboratory scale.⁽¹⁰⁾

2 THERMODYNAMIC STUDY

2.1 Software and Database

A thermodynamic study was carried out using *FactSage* (ver. 6.2) – a ‘thermodynamic software’ described elsewhere by Bale et al.⁽¹¹⁾ The *Equilib* module employed in the determination of the equilibrium state makes use of the ‘Gibbs energy minimization’ method.

The following database Fact53 – FactSage compound database (2010) – allowed performing the simulation. The phase water (as a solution) is included in this database.

2.2 Removal of Phosphorus

A ferrochrome alloy, which forms the basis for the manufacture of stainless steel, must have phosphorus content previously adjusted to low values – as the removal or adjustment of the concentration of this element during the production of stainless steel is difficult and tends to cause a significant loss of chromium to the slag.

During the FeCr alloy production, because of the strongly reducing conditions of the pyrometallurgical process, there is a strong tendency to incorporate most – if not all – of the element P from the raw materials in the FeCr ferroalloy being produced.

Thus, one way to reduce the transfer of phosphorus from ALSI into the alloy is to reduce the content of this component in raw materials; for instance, by leaching.

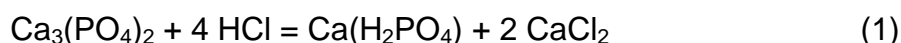
It is known that acidic hydrometallurgical treatments have capacity to transform the insoluble forms of phosphorus in other, which are soluble in water. For the leaching of phosphorus from iron oxides, sulfuric, citric, oxalic and hydrochloric acid have been used. Several research studies in the literature, however, show better results for iron ore dephosphorization when hydrochloric acid is used.⁽¹²⁻¹⁴⁾

In this study, through preliminary tests with ALSI, HCl confirmed to be more effective than H₂SO₄; accordingly, it is the sole acid used in this study.

For the simulation of the ash leaching in an aqueous solution of HCl, one litre of water was used with a varying quantity of HCl. The solution pH was recorded for every amount of HCl tested.

In order to appropriately simulate the phosphorus present in ALSI, calcium phosphate, Ca₃(PO₄)₂, was employed.

The reaction of HCl with tricalcium phosphate can be described by Equation 1.



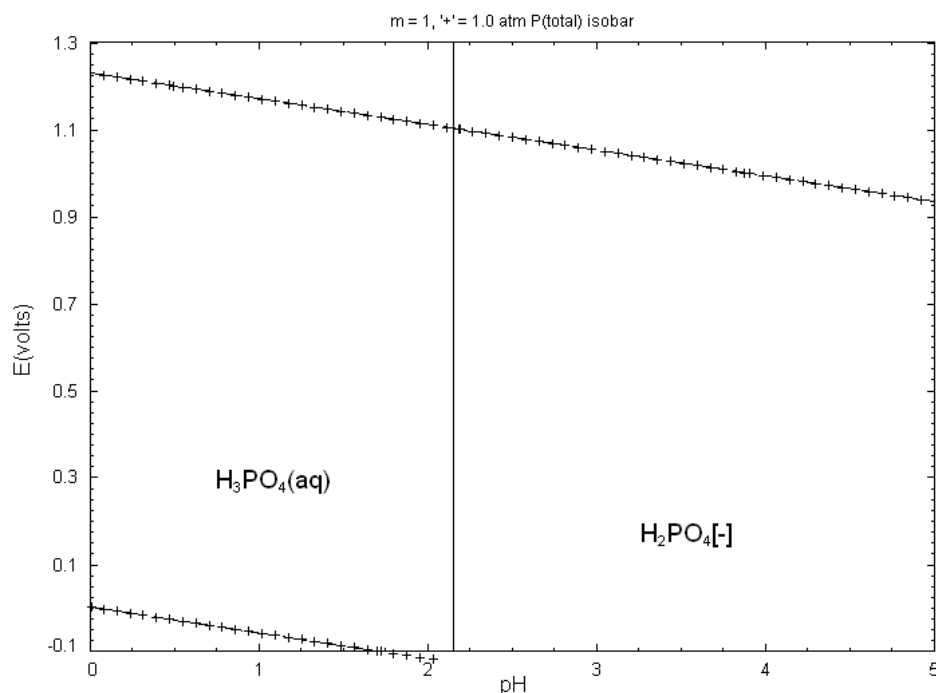


Figure 1. Pourbaix diagram for phosphorous (predominant species as a function of electrochemical potential and pH); concentration m is molality.

This is in agreement with the (predominant) Pourbaix diagram for mildly acid solutions containing P (Figure 1); nevertheless, the predominant species for strongly acid solutions is $\text{H}_3\text{PO}_4(\text{aq})$.

For the P-leaching simulations, the following ionic and aqueous species containing P were taken into consideration: $\text{PH}_3(\text{aq})$, $\text{P}_2\text{O}_7[4-]$, $\text{HPO}_3[2-]$, $\text{H}_2\text{PO}_3[-]$, $\text{HPO}_4[2-]$, $\text{H}_2\text{PO}_4[-]$, $\text{H}_3\text{PO}_4(\text{aq})$, $\text{HP}_2\text{O}_7[3-]$, $\text{H}_2\text{P}_2\text{O}_7[2-]$, $\text{H}_3\text{P}_2\text{O}_7[-]$, $\text{H}_4\text{P}_2\text{O}_7(\text{aq})$.

Furthermore, three different amounts of $\text{Ca}_3(\text{PO}_4)_2$ – 0.01 moles, 0.1 moles and 0.2 moles –, which correspond to 0.62 gram, 6.2 gram, and 12.4 gram P, were added to the water.

As suggested in the literature, simulation results confirm the greater capacity of a solution of hydrochloric acid in water to dissolve P. Relative values, P (aqueous)/ P (total), can express in a concise form the leaching power of the HCl solution (Figure 2).

For the sake of understanding, P (aqueous) expresses the summation of the amounts of this element in each of the P-carrier substance present in aqueous solution, while P (total) expresses the P amount in tricalcium phosphate.

One can state from results, the lower the pH value of solution, the greater the amount of tricalcium phosphate which can dissolve in the HCl aqueous solution; for smaller amounts of $\text{Ca}_3(\text{PO}_4)_2$, higher pH values can suffice to achieve hundred percent theoretical dissolution.

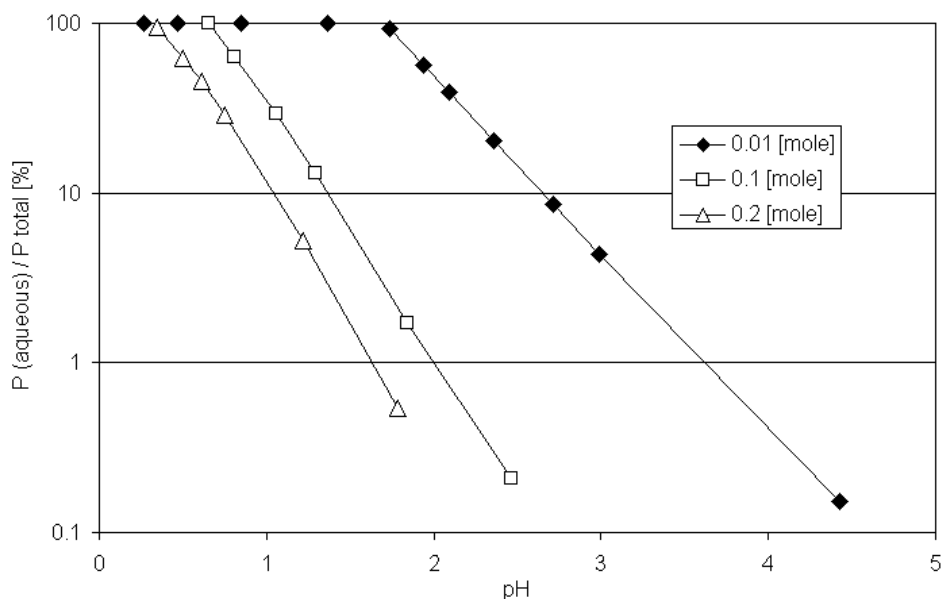


Figure 2. Theoretical percentage of phosphorous dissolved in a solution of hydrochloric acid in water relative to total P, as a function of pH for 0.01 moles, 0.1 moles and 0.2 moles of $\text{Ca}_3(\text{PO}_4)_2$ in 1 [L] water.

3 LEACHING EXPERIMENTS

3.1 Materials and Methods

Ashes from leather shavings incineration used in the present work are from a waste thermal treatment pilot plant of Dois Irmãos city in Brazil.

The ashes were collected in ashtrays of the gasification reactor, ground to particle sizes less than 0.6 mm and stored for further use.

Samples were collected from two incineration batches. Because of the nature of the waste used in the incinerator, they show differences in composition. Their chemical analyses will be shown together with the results of the leaching tests.

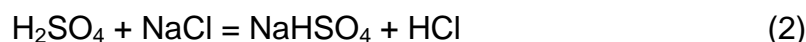
Reagent grade NaCl, hydrochloric and sulfuric acids were used in the experiments.

Preliminary leaching trials with water have shown that P in ash is in the form of substances which are insoluble in pure water – probably inorganic phosphates –, requiring therefore stronger conditions for its removal by leaching.

From a comparison between the sulfuric acid and hydrochloric acid, a clear advantage of the latter could be recognized – as predicted in the literature.

However, considering sustainability and in order to minimize environmental impact, it is necessary to establish a method that is effective both in reducing the phosphorus content of ALSI, as well as in reducing the waste generation – or effluent requiring treatment.

Hydrochloric acid – though more effective – is very volatile, cumbersome to use, and relatively more expensive than the more often used sulfuric acid. In order to overcome these problems, an interesting idea would be to generate it *in situ*, by means of a reaction between sulfuric acid and ‘table salt’ (Equation 2).



With the purpose of testing this, ALSI was submitted to a leaching step with a H_2SO_4 plus NaCl aqueous solution. The procedure was carried out by stirring a mixture of 150 g of ALSI with 10.5 g of NaCl, 45 mL of distilled water, and 22.5 mL of sulphuric

acid for 1 hour at room temperature. Subsequently, the mixture was allowed to rest and aqueous samples were analyzed for P along the time.

3.2 Experimental Results and Discussion

Aqueous samples from the leaching test experiments undertaken with the sulfuric acid solution in the presence of NaCl were analyzed following the Standard Methods for the Examination of Water and Wastewater.⁽¹⁵⁾ Results can be seeing in Figure 3.

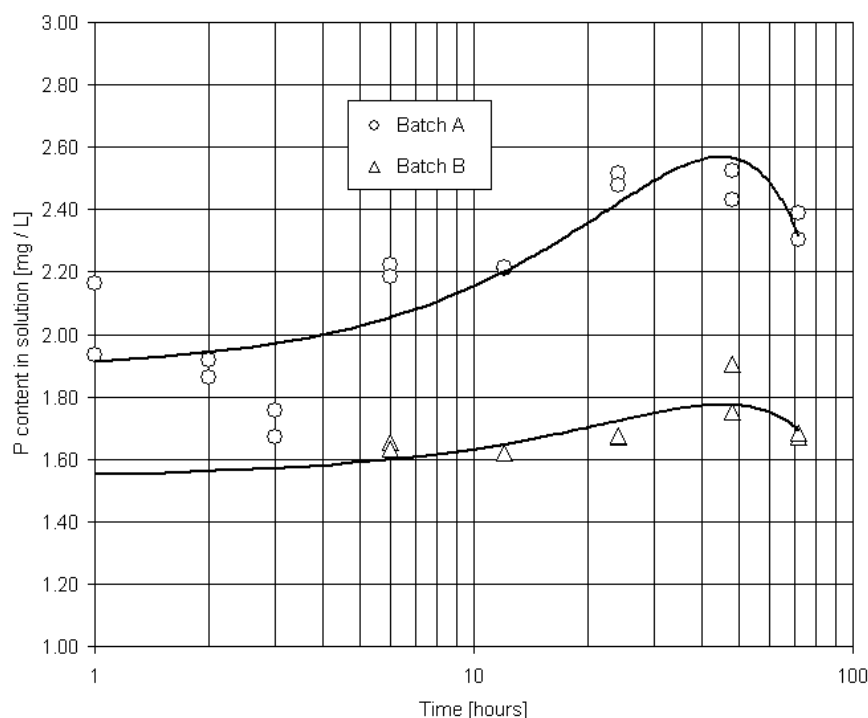


Figure 3. Phosphorous dissolved in a solution of sulfuric acid plus NaCl in water as a function of time; results from two ALSI batches.

Despite some scatter, results show that the content of phosphorus in the liquor for the two batches tested has a certain pattern as a function of time, growing slightly at the beginning but showing a sharper tendency to decline near the end of the experiment. Nevertheless, it can be concluded that the maintenance of the solids for a very long time in contact with the solution may not provide an extraordinary advantage. The reason for this behavior is yet not investigated.

The ash chemical composition results carried out after the leaching tests, made by inductively coupled plasma atomic emission spectroscopy (ICP-AES), for the two batches of waste, including several elements, are given in Table 2. For comparison, the composition of the two ALSI samples before the leaching tests is displayed together.

As it can be seen from the given data, the original content of phosphorus in the two samples is different because of the natural heterogeneity in waste composition. Comparing the results of analyses performed after the leaching experiments with those made before them, a sharp decrease in P level ($P_{final}/P_{initial} \approx 0.45$) can be noticed (some elements show the opposite trend in one or both batches). By comparison of the chromium content, it can be confirmed that the ash mass remains approximately constant, being almost the same before and after the leaching test; mass reduction is in fact ~10%.

Table 2. Chemical composition of ALSI before and after leaching experiments; all figures are given in [wt.%]

Element	Batch A		Batch B	
	Before	After	Before	After
Al	4.96	4.14	3.15	2.46
Ca	1.03	0.67	1.76	1.45
Cr	32.27	32.61	14.26	13.53
Fe	2.39	1.98	2.36	2.07
P	2.47	1.06	1.34	0.62
S	0.31	0.60	1.01	1.68
Si	8.61	9.33	4.98	4.94
Ti	0.30	0.31	3.40	3.56

4 CONCLUSIONS

The thermodynamic simulations and experiments performed in this work demonstrated the possibility of reducing the P content in ashes from incineration of leather shavings, ALSI. This is of importance for the production of HC-FeCr alloy from ALSI by carbothermic reduction because of the detrimental effect of phosphorus in steels.

These results open new perspectives for the disposal of waste from leather tanning and leather goods processing, which include both the thermal treatment of waste (with energy recovery) as well as the recycling of metal chromium from ashes. They are, however, not definitive; this will be explained next.

Because of the high reducibility of P contained in ash, it passes fully into the bath. Since the Cr content in ash is smaller than the Cr content in the alloy, it is easy to understand that P in raw material must be very low in order to satisfy the extremely low content of P in the ferroalloy (ca. 0.03 wt.%).

Harsh leaching conditions may be effective in eliminating P. However, leaching tests conditions described in this work can be considered as very mild. There are strong reasons, though, for this choice, e.g., less possibility of undesirable side effects – like the leaching of valuable Cr – and favorable economics. Main motivations for the mild conditions applied here are, unfortunately, overshadowed by the low P reduction rating in ash.

So, harsher leaching conditions should be used to improve P solubility. And, last but not least, in an extreme case, the ferroalloy should be subjected to a supplementary pyrometallurgical process with special slags in order to further reduce the P content in the ferroalloy.

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