PRODUCTION OF HIGH CARBON FERROCHROMIUM ALLOY FROM FOOTWEAR LEATHER WASTE ASH THROUGH A CARBOTHERMIC REDUCTION

by
B. M. WENZEL[1,2]*, N. R. MARCILIO[1]*, J. L. KLUG[3], N. C. HECK[3], AND M. GODINHO[4]
[1]*Laboratory of Waste Treatment (LPR), Department of Chemical Engineering, Federal University of Rio Grande do Sul (UFRGS),*
PORTO ALEGRE, RS, BRAZIL.

[2]*Federal University of Fronteira Sul (UFFS),*
CERRO LARGO, RS, BRAZIL.

[3]*NTCm, Department of Metallurgy, UFRGS,*
PORTO ALEGRE, RS, BRAZIL.

[4]*Department of Chemical Engineering, University of Caxias do Sul (UCS),*
CAXIAS DO SUL, RS, BRAZIL.

ABSTRACT

The majority of hazardous solid waste generated in "Rio Grande do Sul" State, Brazil, is produced from footwear leather industry. Thermal treatment leather waste is considered as a good alternative to deal with this problem, by generating energy. It is also possible to recover chromium from the ash generated during incineration. The aim of this work is to evaluate high carbon ferrochromium alloy production from leather waste ash, through computational and laboratory analysis. Computational thermodynamics was used to simulate ash Cr_2O_3 carbothermic reduction and to determine composition of the laboratory alloys. Several runs were done using a laboratory furnace at 1600°C to get ferrochromium alloys from the ashes. Different kinds of analyses were done to determine alloys and slags compositions. It was demonstrated that it is possible to use the chromium from leather waste ash for a production of high carbon ferrochromium alloy through carbothermic reduction at 1600°C. The results obtained showed a new opportunity for hazardous solid waste management of the leather industry, in the context of energy generation from combustion of leather waste. The computational thermodynamics simulations presented good agreement with experimental results.

RESUMEN

La mayoría de los residuos sólidos peligrosos generados en el estado de Rio Grande do Sul, Brasil, es producido por la industria de calzado de cuero. El tratamiento térmico de los residuos de cuero se considera como una buena alternativa para hacer frente a este problema, mediante la generación de energía. También es posible recuperar cromo de la ceniza generada durante la incineración. El objetivo de este trabajo es evaluar la producción de una aleación de ferrocromo con alto contenido de carbono a partir de las cenizas residuales del cuero, a través de análisis computacional y de laboratorio. La termodinámica computacional fue utilizada para simular cenizas de Cr_2O_3 por reducción carbotérmica y para determinar la composición de las aleaciones de laboratorio. Varias corridas se realizaron utilizando un horno de laboratorio a 1600°C para obtener aleaciones de ferrocromo de las cenizas. Diferentes tipos de análisis se realizaron para determinar las composiciones de las aleaciones y de las escorias. Se demostró que es posible utilizar el cromo de la ceniza de los residuos de cuero para una producción de alta aleación de ferrocromo de alto contenido de carbono a través de la reducción carbotérmica a 1600°C. Los resultados obtenidos mostraron una nueva oportunidad para la gestión de los residuos sólidos peligrosos de la industria del cuero en el contexto de la generación de energía a partir de la combustión de los residuos de cuero. Las simulaciones computacionales termodinámicas presentaron una buena concordancia con los resultados experimentales.

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*Corresponding authors' e-mail addresses: bruno.wenzel@uffs.edu.br (B.M. Wenzel); nilson@enq.ufrgs.br (N.R. Marcilio);
Tel.: +55 51 3308 3956.

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INTRODUCTION

According to Brazilian governmental institutions (State Foundation of Environmental Protection – FEPAM), in "Rio Grande do Sul" State of Brazil, 118 million ton/year of hazardous solid waste from leather industry are generated – 62% of total hazardous wastes.[1] This solid waste is hazardous since it contains trivalent chromium derived from salts used to tan hides. The majority of it is disposed in landfills and only about 3% is recycled.[1]

Thermal treatment can be applied to solve this problem, producing energy as a by-product from the heat, which is generated in the combustion process. As a result of the thermal treatment application, an ash with high chromium content is also produced. In recent times a semi-pilot unit (350 kWth), projected at Federal University of "Rio Grande do Sul", was built to study leather residue gasification and combustion.[2, 3] Thermal capacity of this unit is going to increase in the next future reaching a higher level of 600 kWth.

The produced ash during the thermal treatment process contains 50-62 wt% Cr_2O_3 [2, 4-7] and $Cr^{+6} < 400$ ppm.[2, 5, 7] This ash can be used to produce high carbon ferrochromium alloy (Fe-Cr-HC).

Ferrochromium alloys are used at steelworks plant as an input for different qualities of steels, such as stainless steel. Production of a ferrochromium alloy is related to a pyrometallurgical process in which the slag phase plays an important role.[8, 9] For chromium containing slag changes in oxygen pressure noticeably affect their composition due to the multi-valence state of chromium ions.[10, 11]

The aim of the present work is to evaluate production of high carbon ferrochromium alloy from leather waste ash in laboratory tests using high temperature furnace. Different experimental conditions were evaluated and the results compared with computational thermodynamics simulations. This evaluation was made by controlling the carbothermic reduction process at 1600°C. The simulations of the present work are focused on the equilibrium aspects of the chromium oxide reduction, by assuming that the thermodynamic approach establishes the direction of the chemical reactions. Limiting conditions are neglected.

METHODOLOGY

Materials

The ash used in the present work was collected in the gasification reactor of the semi-pilot plant that was built to process leather waste by thermal treatment process (gasification and combustion). The semi-pilot plant is described in details elsewhere.[2, 3] Representative ash samples were picked up through successive manual quartertones. The samples were comminuted in a ball mill to particle size < 75mm.

TABLE I
Ash composition determined by XRF.

Compound/element	wt%
CHN	0.18
SiO_2	9.96
Al_2O_3	6.59
TiO_2	8.41
Fe_2O_3	2.31
CaO	4.43
CuO	0.06
P_2O_5	2.58
Cr_2O_3	62.29
K_2O	0.86
Cl	0.01
SO_4	2.32
Total	**100.00**

Ash composition is shown in Table 1 where quantitative X-ray Fluorescence Spectroscopy (XRF) analysis is presented for inorganic elements. The carbon (0.03%), hydrogen (0.04%) and nitrogen (0.11%) contents are showed as a sum of these elements (CHN), and were determined according to ASTM D5373.[12]

Besides ash samples the following materials were used to accomplish the experimental work: graphite (98% C); calcium oxide (95% CaO); metallic iron (99% Fe); silicon oxide (99% SiO_2); alumina crucibles (99.7% Al_2O_3).

Experimental Procedure and Apparatus

The experimental apparatus consists of a 6.5 kW cylindrical furnace coupled with a temperature controller, see Figure 1. Argon is injected in furnace through a 7mm alumina tube, above the crucible (containing ash and other supplies).

Laboratory runs were performed to evaluate the carbothermic reduction of the Cr_2O_3 contents of the ash, which was mixed with others materials, such as calcium oxide, silicon oxide, metallic iron and graphite. The goal was to obtain a similar product to an industrial high carbon ferrochromium alloy in laboratory scale. The specification of industrial high carbon ferrochromium alloy, grade A, which was used in the present work was as follows: 51.0-56.0% Cr, 6.0-8.0% C, 6.0% Si (maximum), 0.030% P (maximum), 0.040% S (maximum).[13]

Eight experiments were performed in argon atmosphere[11, 14, 15] in the apparatus presented in Figure 1 (see Table 2) at 1600°C.[8, 9, 11, 16, 17] Run 1 and 2 were performed under identical conditions to verify repeatability of the experimental apparatus. The mixture total mass used in Run 2 was six times higher than that in Run 1 (Run 1 = 68.63 g; Run 2 = 411.81 g).

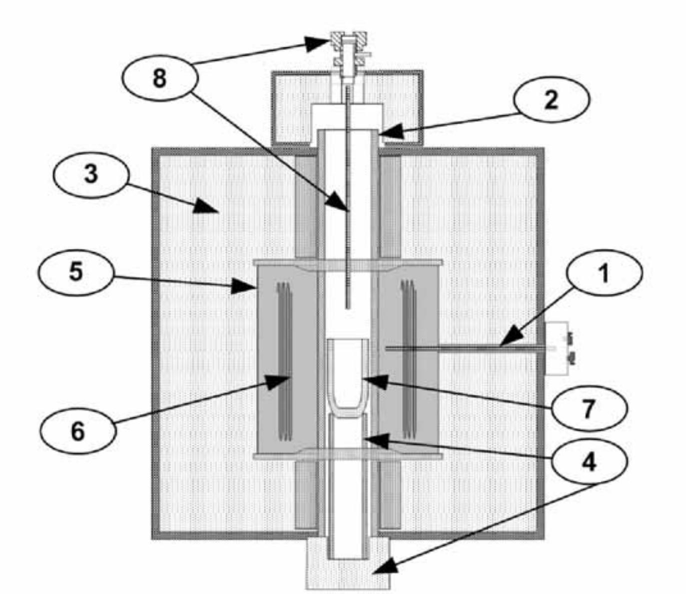

Figure 1. Schematic diagram of the furnace used for the experimental work. 1. thermocouple; 2. alumina tube; 3. refractory; 4 . crucible ceramic support; 5. heating chamber; 6. heating element (MoSi2); 7. crucible; 8. inert gas entry.

The applied experimental procedure was as follows: ash and inputs (calcium oxide, silicon oxide, metallic iron and graphite) were mixed and put in the Al_2O_3 crucible in the furnace, where the argon injection of 5 NL/min was set up. Further, heating at 10°C/min from ambient temperature up to 1400°C; heating at 5°C/min from 1400°C up to 1600°C; maintenance at 1600°C during 2h; cooling at 5°C/min from 1600°C up to 1400°C; cooling at 3°C/min from 1400°C up to 1100°C; natural cooling from 1100°C up to ambient temperature was performed. The initial compositions and experimental parameters for each run are shown in Table 2. Basicity (%CaO/%SiO_2) was in the range 0.5-2.5.

After carbothermic reduction, alloy and slag were separated and comminuted in a planetary ball mill. In Table 3 are presented the techniques, which were used to characterize alloy and slag for the eight runs. The obtained slag was analyzed through XRF technique. The compositions of produced alloys were identified by applying the following techniques: Graphite Furnace Atomic Absorption Spectrometry Analysis (GF-AAS); Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES); Combustion-Infrared Spectrophotometer, Leco CS 244 equipment (LECO).

For GF-AAS and ICP-OES analysis the digestion methodology described in[18] was executed in triplicates.

Thermodynamic Simulations

The production of a high carbon ferrochromium alloy from leather waste ash was simulated through computational thermodynamics. For all the equilibrium calculations thermodynamic systems containing a slag phase, a liquid iron phase and a gas phase (O_2, CO and CO_2) were considered at a temperature of 1600°C.

Two different systems – System 1 and System 2 – were used for the simulations considering inputs as follows: leather waste ash, calcium oxide, silicon oxide, metallic iron and graphite:

- System 1: CaO, SiO_2, Al_2O_3, CrO, Cr_2O_3, SO_4, Fe, C;
- System 2: CaO, SiO_2, Al_2O_3, CrO, Cr_2O_3, SO_4, Fe_2O_3, TiO_2, CuO, P_2O_5, K_2O, Fe, C.

The software employed in the present work is FactSage version 5.5. It contains the module Equilib, which minimizes the Gibbs energy of the system and calculates the concentrations of chemical species at the state of thermodynamic equilibrium from elements or compounds selected as input.[19] The following databases [20-25] were used in the present work:[26]

- FToxid solution database (FToxid53Soln.sda) contains oxide solutions. For example, the molten slag phase contains CaO-SiO_2-Al_2O_3-CrO-Cr_2O_3 where all available data have been fully optimized. The aforementioned "System 2" contains several oxides. According to FactSage database documentation [26] the FToxid databases contain data for pure oxides and oxide solutions of 20 elements. It has to be noted that not all binary and ternary sub-systems have been evaluated and optimized, as well as not all composition ranges were covered. Sub-systems, which have not been evaluated and optimized have been assumed ideal or have been approximated.
- FToxid compound database (FToxid53Base.cdb) contains stoichiometric solid and liquid oxide compound evaluated and optimized to be thermodynamically consistent with the FToxid solution database.
- FSstel (FSstel53Base.cdb) database is intended to provide a basis for calculations covering a wide range of steelmaking processes. From this database the phase "Fe-LIQUID" was used in the present work.

TABLE II
Runs initial compositions (wt%) and experimental parameters of the tested mixtures (before carbothermic reduction).

Reactant	Source	Run							
		1	2	3	4	5	6	7	8
Cr_2O_3 (%)	Ash	45.38	45.38	42.67	42.22	31.92	31.47	31.88	32.01
Fe_2O_3 (%)	Ash	1.68	1.68	1.58	1.57	1.18	1.17	1.18	1.19
SiO_2 (%)	Ash and silica	7.26	7.26	6.83	6.75	18.45	18.19	14.73	24.66
CaO (%)	Ash and calcium oxide	12.05	12.05	17.01	16.83	18.45	18.19	22.10	12.33
Al_2O_3 (%)	Ash	4.80	4.80	4.51	4.46	3.38	3.33	3.37	3.38
TiO_2 (%)	Ash	6.13	6.13	5.76	5.70	4.31	4.25	4.30	4.32
CuO (%)	Ash	0.04	0.04	0.04	0.04	0.03	0.03	0.03	0.03
P_2O_5 (%)	Ash	1.88	1.88	1.77	1.75	1.32	1.30	1.32	1.33
K_2O (%)	Ash	0.62	0.62	0.59	0.58	0.44	0.43	0.44	0.44
Cl (%)	Ash	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
SO_4 (%)	Ash	1.69	1.69	1.59	1.58	1.19	1.17	1.19	1.19
Fe (%)	Iron	9.03	9.03	8.49	8.40	6.35	6.26	6.34	6.37
C (%)	Graphite	8.61	8.61	8.10	9.04	11.62	12.84	11.60	11.65
Experimental Parameter									
Basicity (CaO/SiO_2)		1.7	1.7	2.5	2.5	1.0	1.0	1.5	0.5
Ratio ($CaO+SiO_2$)/ (Cr_2O_3 + Fe_2O_3)		0.41	0.41	0.54	0.54	1.11	1.11	1.11	1.11
Carbon (% of stoichiometric amount[a])		-22.7	-22.7	-22.7	-12.8	48.3	66.2	48.3	48.3

[a] according to the following reactions: $Cr_2O_3 + 3\ C \rightarrow 2\ Cr + 3\ CO$ and $Fe_2O_3 + 3\ C \rightarrow 2\ Fe + 3\ CO$.

- FACT53 (FS53Base.cdb) contains data for more than 4500 compounds (pure substances) from standard compilations as well as most of the data for those compounds which have been evaluated and optimized to be thermodynamically consistent with the FToxid solution database.

RESULTS AND DISCUSSION

the main goal of the present work was to obtain an alloy similar to an industrial high carbon ferrochromium alloy. In Figure 2 are shown some of the produced alloys. As can be seen, the alloys presented shiny metallic phase, which can be easily comminuted.

Equipment Reproducibility

In Table 4 are shown the mean, standard deviation and variation coefficient of XRF measurements of slag phase of runs 1 and 2. It can be noted that the experimental apparatus presented good reproducibility of experiments, and the strong reduction condition assumed in simulations was obtained.

Chromium

In Figure 3 chromium content of the alloys in runs 2 to 8 is shown. This is a visualization of the comparison between thermodynamic (System 1 and System 2, calculated through computational thermodynamics according to item 2.1) and experimental results (GF-AAS). A good correlation between them was found.

TABLE III
Techniques applied to characterize the samples after carbothermic reduction.

Run	Slag	Alloy		
	XRF	GF-AAS (Cr)	ICP-OES (P, Ti and Si)	LECO (C and S)
1	X			
2	X	X	X	
3	X	X	X	
4	X	X	X	
5		X		X
6		X		X
7		X		X
8		X		X

Figure 2. Alloys produced in laboratory scale.

The experimental results are presented considering the relative error (95% degree of confidence) of the analyses. The chromium content of the alloys obtained in laboratory scale was similar to that one described in the specification of the industrial alloy. In Figure 4 are presented the slags chromium content (liquid + solid phases), experimental (XRF) and calculated (computational thermodynamics) results. As can be seen, a good correlation between thermodynamic and experimental results was found in terms of slags chromium content.

TABLE IV
Mean, standard deviation and variation coefficient of slag composition (Runs 1 and 2) by quantitative XRF analysis.

Element	Mean	Standard deviation	Variation coefficient (%)
Si	3,03	0,22	7,26
Al	10,98	0,54	4,87
Ti	4,52	0,12	2,55
Fe	4,14	0,05	1,21
Ca	17,73	0,37	2,09
P	0,16	0,07	41,94
Cr	28,42	0,18	0,62

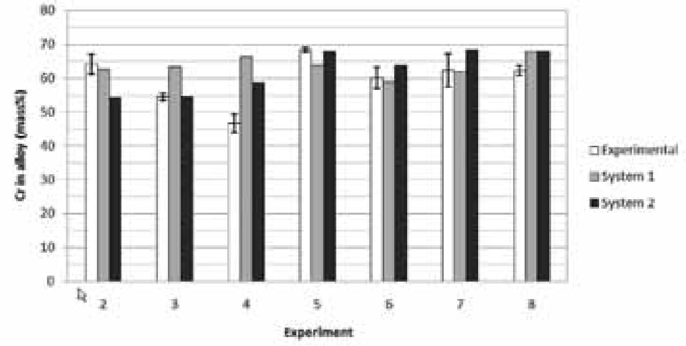

Figure 3. Alloys chromium content compared with thermodynamic simulations (Systems 1 and 2).

Phosphorus

Well know fact is that the control of phosphorus content during steel production is critical because phosphorus affects mechanical properties of steel. The appropriate phosphorus content for several qualities of steels lays usually around 0.03%. Thus, phosphorus content of a ferrochromium alloy must be kept at a low level. Figure 5 shows phosphorus content of the alloys, Runs 2 to 4, regarding thermodynamic simulations (System 2) and experimental results (ICP-OES). A very good correlation between the simulated results and the experimental results was also obtained.

The phosphorus content of the alloy was high according to the industrial high carbon ferrochromium alloy specification. The upper phosphorus limit is set to 0.030% P.[13]

It is difficult to maintain the phosphorus of the leather waste ash in the slag phase through the carbothermic reduction process, because during these conditions phosphorous is promptly transferred from the slag to the metal phase. Further research is needed to develop a method for the phosphorous contents extraction from leather waste ash before the pyrometallurgical process of reduction. In the work of the author[27] it was reported that 95% of the phosphorus content in iron ore can be removed through an treatment with nitric acid solution.

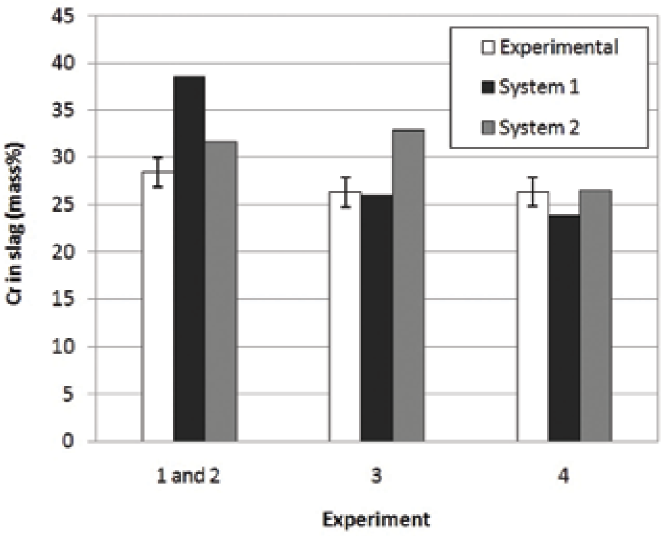

Figure 4. Slags chromium content (liquid + solid phases), experimental and calculated (computational thermodynamics) results.

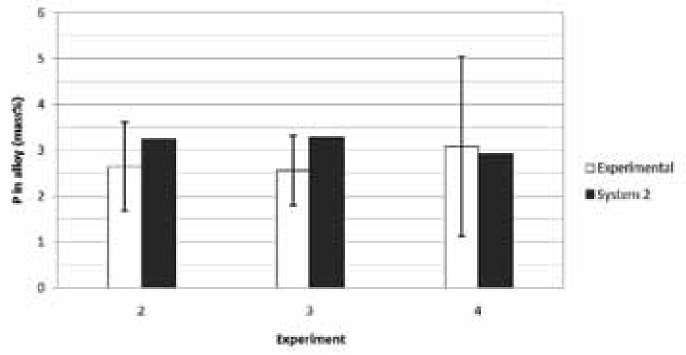

Figure 5. Phosphorus content of the laboratory alloys compared with thermodynamic simulations (System 2).

The aforementioned phosphorus reduction is significant. In these conditions, using 146 kg of leather waste ash there is a potential to obtain 100 kg of an alloy containing 50% Cr and 0.35% P. Further, by using 100 kg of this alloy as input in a steelworks plant, one ton of steel containing 5% Cr and 0.035% P (which is an adequate phosphorus content for many steel qualities) could be produced.

Sulphur

Sulphur is also a chemical element with high importance because its presence in the steel affects the mechanical properties. Sulphur content in the alloys was determined in Runs 5 to 8 by means of a LECO analyzer (see Figure 6). These values are higher than the maximum limit (0.025 %S).13 This problem can be overcome by controlling process reduction conditions.

Silica

Silica maximum content in the high carbon ferrochrome alloy is 5% Si.[13] In this work, Si contents of produced alloys were lower than 0.0014% (ICP-OES – Runs 2, 3 and 4). Similar results were obtained through computational thermodynamics simulations. Thus, silicon level remains in the slag phase as it is shown in Figure 7, where %Si of the slag was determined by using XRF in combination with thermodynamic simulations results.

Carbon

Carbon content in the alloys in Runs 5 to 8 was determined by means of a LECO analyzer (see Figure 8). It was found that the carbon content varied in the range of 4.0-6.0% C. In the industrial specification this element present in the range of 6.0-9.0% C.[13]

Thermodynamic simulations indicate a carbon content of the alloy higher than these determined experimentally. This fact can be explained by considering computational thermodynamics simulations of a closed system. In the experimental set up presented in Figure 1, carbon losses of gaseous compounds such as CO and CO_2 were possible.

Other Elements

Besides the aforementioned elements, related to an industrial specification[13] the contents of other elements were also

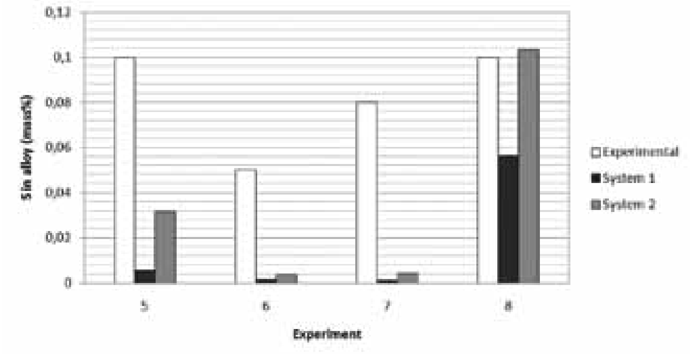

Figure 6. Sulphur content of the laboratory alloys compared with the thermodynamic simulations (Systems 1 and 2) results.

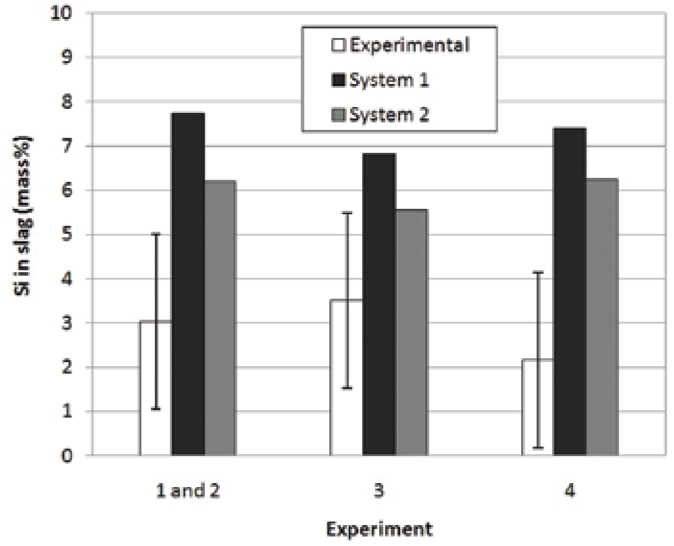

Figure 7. Silica content of the slags (liquid slag + solid oxides): experimental and calculated (computational thermodynamics) results.

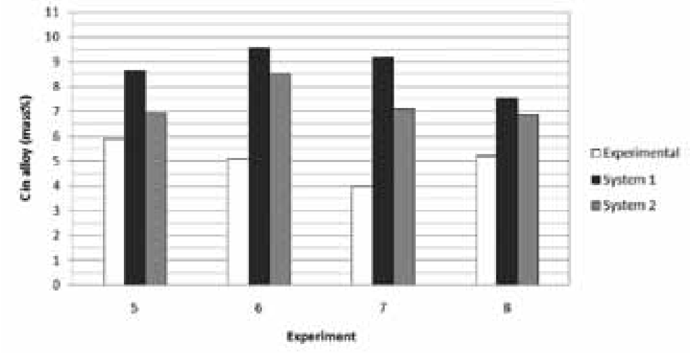

Figure 8. Carbon content of the laboratory alloys compared with thermodynamic simulations (Systems 1 and 2) results.

determined. Ti content of the alloy in Runs 2, 3, and 4 was determined to be 0.39, 0.19 and 0.93 mass%, respectively (ICP-OES). In Figure 9, Fe, Ca, Al, and Ti contents in the slags (determined through XRF) are compared with thermodynamic results (Systems 1 and 2).

In spite of the conditions provided by carbothermic reduction and predicted by thermodynamic results, iron content determined in the slags is relatively high. In the initial compositions of the mixtures (before carbothermic reduction), iron contents were in the range of 1.18-1.68% Fe_2O_3 (see Table 2). After reduction iron contents of the analyzed slags were around 3-4% Fe (see Figure 9).

Conversion

The experimentally obtained conversion was calculated for runs 1 to 4, through a global mass balance and the chromium mass balance. In runs 5-8 the total mass of alloy was estimated by applying the following consideration: alloy phase is formed for Cr, C, S, P and Ti; total content of P was reduced in metallic phase; and the Ti content in alloy correlated with simulation results of "system 2". The basis of these assumptions was the fact that some part of the metal presented in the crucible wall, which affected the exact mass measurement of obtained alloy.

In Fig. 10 is shown the conversion of chromium oxide to metallic chromium as a function of the basicity. Analysis of the literature data [11] proved that the slag basicity (g CaO/g SiO2) can influence a chromium recovery from the system $CaO-SiO_2-CrOx$ at 1600°C and in strong reducing conditions – since variation at basicity can alters activity values of the chromium ions of the liquid slag (Cr^{+2} and Cr^{+3}). With a rising basicity was observed a decrease of divalent chromium fraction and an increase of chromium oxides activities (in liquid slag). This observation suggested that a utilization of high basicity slags is followed by an increasing activity of chromium oxides. It means chromium recovery would be maximized during ferrochromium alloy production. In Fig. 10a, the increase of slag basicity presents an increase of experimental chromium conversion. Comparison of Fig. 10a

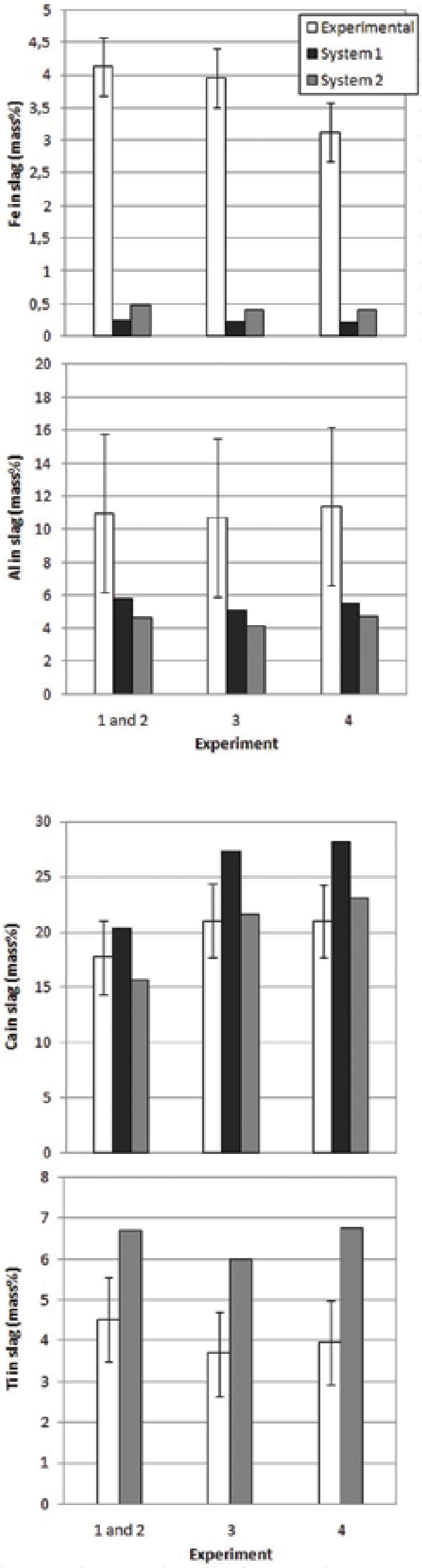

Figure 9. Metals (Fe, Ca, Al and Ti) in slag (liquid slag + solid oxide): experimental and thermodynamic simulations (Systems 1 and 2) results.

and 10b shows the effect of ratio $(CaO+SiO_2)/(Cr_2O_3+Fe_2O_3)$ (Rox) in chromium conversion. In Fig. 10b, simulations results indicate high conversion, however the experimental results do not confirm this tendency. Probably by liquid slag phase, predicted in simulation results, not was formed in practice.

Fig. 11 shows the effect of carbon quantity in the conversion of chromium. In Fig. 11a the insufficient quantity of carbon is observed when the conversion and carbon content increased. Fig. 11b shows a decrease of conversion with increase of carbon. This fact is due to the formation of chromium carbides, which is predicted by simulations results.

CONCLUSIONS

In a laboratory scale was proven that the method of chromium utilization from leather waste ash was suitable for a production of high carbon ferrochromium alloy, through a process of carbothermic reduction at 1600°C. Computational thermodynamics was used as a powerful tool to design experiments related to carbothermic reduction by maximizing chromium content of the alloys. A correlation between thermodynamic simulations and experimental results was demonstrated. In addition to this, it was observed that the "System 2" correlated better with experimental data than the "System 1". Phosphorus content of the alloys obtained through a carbothermic reduction is above its upper limit according to high carbon ferrochromium alloy specification. Further research is currently under way, in order to achieve a cost effective method for phosphorus removal from leather waste ash before set up of the pyrometallurgical process. The obtained results clearly showed a new possibility for hazardous solid waste utilization in the context of energy generation from combustion of leather wastes.

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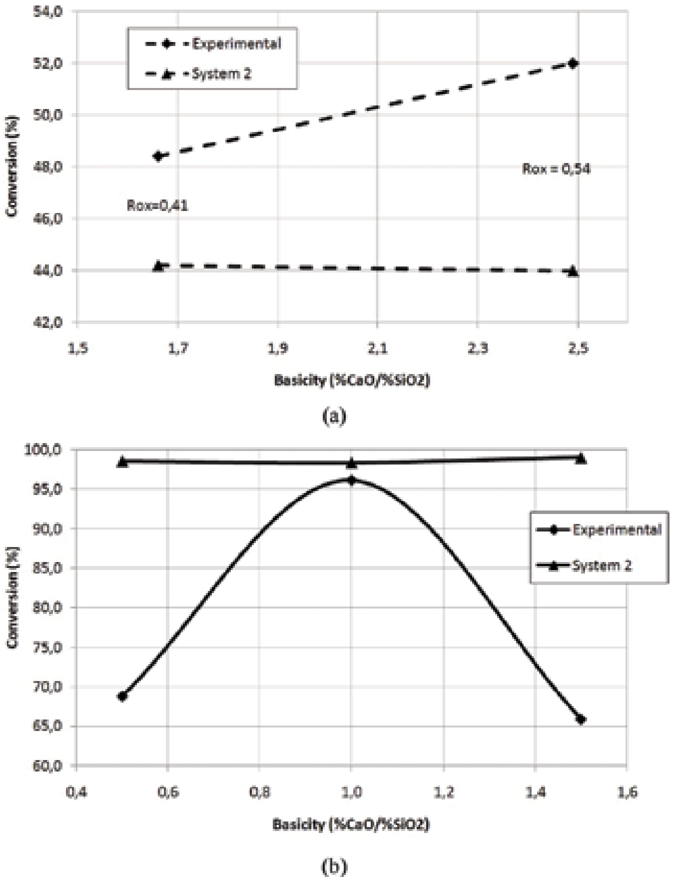

Figure 10. Effect of basicity in conversion of chromium from metallic phase. (a) Runs 2 and 3 (Rox=0.41 and 0.44); (b) Runs 8, 5 and 7 (Rox=1.11).

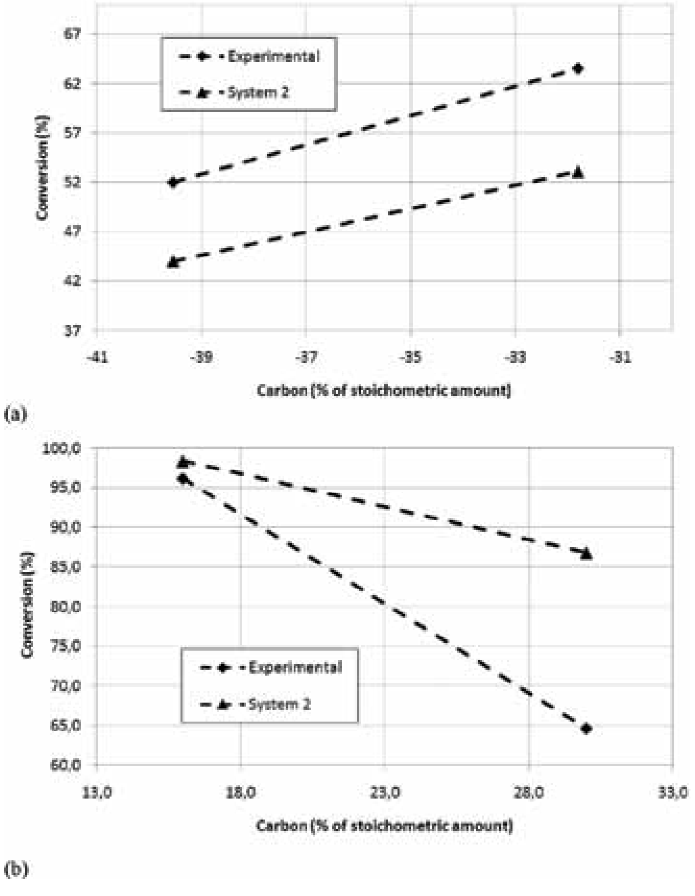

Figure 11. Effect of carbon content on the conversion of chromium. (a) Runs 3 and 4; (b) Runs 5 and 6.

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