

REDUCTIVE SMELTING OF GREEK BAUXITE RESIDUES FOR IRON PRODUCTION

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Abstract

The reductive smelting of Greek bauxite residues was investigated for the production of an iron product that meets some crucial industrial requirements as a blast furnace feed. Fine-grained Greek bauxite residue - either as is or in the form of pellets - and solid fuel reducing agents -lignite and coke-, were used as raw materials. The effect of parameters such as the smelting temperature, the amount of the reducing agent in the mixture, the retention time and the addition of fluxes on the quality of the metallic product, as well as the basicity and the desulfurization capability of the slag, was investigated. The results obtained regarding the chemical properties of the metallic product were very promising, providing input for further research on the optimization of the proposed pyrometallurgical method for the production of an attractive ferrous raw material for the iron ore industry.

Introduction

The application of various processing methods for the effective recovery of major metallic constituents of bauxite residues, has been a matter of scientific interest by numerous researchers [1]. The current work constitutes a part of an integrated research effort which aims to investigate alternative ways of utilizing bauxite residue as a raw material in the iron ore industry, by applying pyrometallurgical treatment methods. Within this framework, roasting reduction, magnetic separation for iron enrichment and pelletization of the Greek bauxite residue have already been investigated [2, 3]. The present study is focused on the reductive smelting of the same raw material for iron production.

The crucial technical requirements that determine the usability of an iron-bearing raw material for the iron ore industry -either as a feed for a rotary kiln or a blast furnace-, are the following: iron content, "gangue constituents" (SiO₂, CaCO₃, MgO, Al₂O₃), "deleterious impurities" (S, P, Na₂O, K₂O and TiO₂), physical properties (porosity, durability, ore structure), reducibility and its amenability to concentration. Given that about 1.61 tonnes of iron ore with an iron content of 60% are required for the production of each tonne of cast iron, and also considering the fact that iron ore prices have almost quadrupled since 2004, it is easy to understand how crucial it is for the industry to make use of an iron bearing raw material with a lower iron content (20-30% Fe) which can substitute part of the iron ore feed. The iron content of bauxite residue, mainly in the form of iron (III) oxide, ranges from 30 to 50%, while at the same time the typical content of gangue material -such as CaO and Al₂O₃ - is such that this does not seriously affect its melting point. Thus, much attention has been focussed towards iron recovery in these residues.

Reduction smelting constitutes the most significant pyrometallurgical process for the production of cast iron. It is mainly conducted in blast furnaces or electrical furnaces. Many efforts in the smelting reduction of bauxite residue material

have been reported [4, 5, 6]. The most common reducing agent utilized is coke while the iron recovery finally obtained is always over 90%.

Experimental

The sample of bauxite residue utilized in the present study was provided by the Greek alumina refinery owned by Aluminum of Greece S.A. It is a fine grained material, given that a percentage of 40% by weight is less than 2 μm. Lignite and coke were used as reducing agents. Chemical analysis of the raw materials is given in Table I. The total iron (Fe^{tot}) content in the bauxite residue is about 33.5%, which is indicative of the fact that it constitutes an important potential iron source for the iron ore industry. Its main mineral constituents, as determined by mineralogical analysis conducted by X-Ray diffraction, were hematite, gibbsite, diaspore, calcite and hydroxysodalite.

Table I. Chemical Analysis of Greek Bauxite Residue and Reducing Agents

Component	Bauxite residue (%)	Lignite (%)	Coke (%)
Fe ₂ O ₃	48	4.44	29.09
Na ₂ O	3.26	2.83	2.67
SiO ₂	6.96	53.81	
CaO	14.84	4.91	0.5
MgO	0.24	3.39	2.9
Al ₂ O ₃	15.85	19.11	
K ₂ O	0.07	0.69	
TiO ₂	7.06	0.79	
CO ₂	2.24	3.78	
SO ₂	0.78		
L.O.I. C ^{fix}	11.37		
Ash		30.1	81.7
		20.1	5.0
Volatile Matter		49.75	13.3

Moreover, a single experiment was conducted regarding smelting reduction of bauxite residue in form of pellets with lignite (bauxite residue/lignite: 1/3 by weight and bentonite: 0.6% by weight as a binding agent).

The melting temperature of the bauxite residue was initially determined with a LECO AF 600 apparatus, by employing the Seger cones technique, based on the determination of four characteristic temperature values: the start of softening, end of softening, start of melting and end of melting points. The melting point of the bauxite residue was determined to be 1400°C, as a mean of five values. The determined value is in agreement with the theoretically calculated value from the ternary phase diagram of FeO - CaO - Al₂O₃ (the Fe₂O₃ content of the bauxite residue is stoichiometrically converted to FeO content).

The smelting reduction experiments were conducted in two types of laboratory furnaces:

i) Electric resistance heating furnace Tamman (Figure 1) (60 KVA, T_{max} : 2500°C): its main part is a cylindrical heating tube made of carbon material, surrounded by a thermal insulating material, so that the inside of the heating tube acts as a heat treatment chamber, in which the graphite sample holder is placed. The temperature was recorded by a Raytek optical sensor pyrometer (laser).

ii) Induction smelting furnace (Figure 2): This consists of an induction heating system, a water cooled induction coil, a supporting body having a suitable circumference for supporting a graphite crucible. The temperature during the experimental procedure was measured by the same Raytek optical sensor pyrometer.

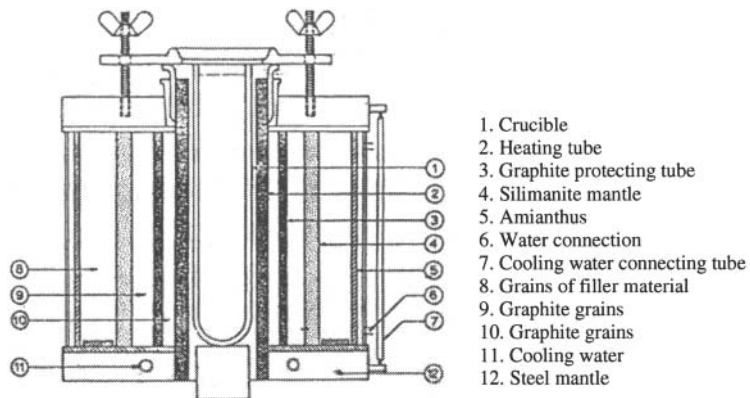


Figure 1. Electric resistance heating furnace Tamman

Results and Discussion

The effect of the following parameters on the final result of smelting reduction was investigated: temperature, retention time of the smelted material, bauxite residue/lignite ratio and the addition of fluxes. The determination of the bauxite residue/lignite ratio was based on the stoichiometrically required quantity of carbon required for the complete reduction of Fe_2O_3 to metallic iron. Moreover, the addition of fluxes (CaO and SiO_2 reagents), was based on the theoretical determination of the desirable lower melting point, according to the ternary phase diagram of Al_2O_3 -CaO- SiO_2 , taking into consideration that the aforementioned are the three basic constituents of the bauxite residue slag. Thus, the addition of three different ratios of CaO and SiO_2 was investigated per 100 g of the mixture bauxite residue/lignite (4/1 by weight): i) SiO_2 -CaO: 20-0 g, ii) SiO_2 -CaO: 35-5 g, iii) SiO_2 -CaO: 62-38 g.

The experimental conditions of reduction smelting as well as the chemical analysis of the metallic products, are presented in Table II. The most important conclusion deduced is that regardless of the conditions employed, a metallic product with iron and carbon content ranging from 91.3-95.8% and 2.4-5.4 % respectively, was produced. The quality of iron produced can be characterized as satisfactory, since according to a typical analysis of cast iron, the iron content is approximately 94% and carbon content fluctuates between 3.5-4.5%. In Figure 3, the effect of the ratio of bauxite residue/lignite on mixture melting point is presented. It is noted that increase of the aforementioned ratio results in a considerable increase of the melting temperature.

The sample fed in both furnaces was 70-80 g. It is noted that two types of furnaces were used for the conduction of smelting reduction of experiments, due to the fact that each one has several advantages and disadvantages. It is noted that the determination of temperature was more precise in the experiments conducted in the Tamman furnace, however, the duration of each experiment was more than 4 hours in Tamman and only half an hour in the induction smelting furnace. Nevertheless, due to the intense eddying of the material resulting from the Foucault current, there was loss of fine material and therefore, it was difficult to conduct mass balance calculations.

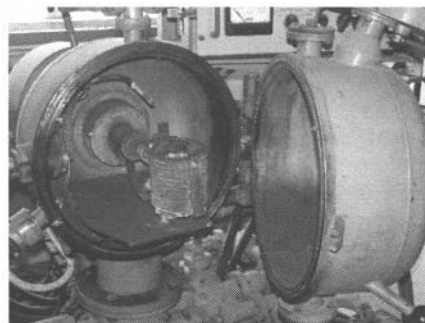


Figure 2. Heating chamber of the induction smelting furnace

In Figure 4 the effect of the type of the reducing agent and reaction time on carbon content in the pig iron is given. It is seen that increase of the retention time of the bauxite residue melt results in a significant decrease of the carbon content. Moreover, after 15 minutes of smelting reduction, the carbon content of the metallic product fluctuates between 4.6-5.1%, while after 45 minutes the respective values are 2.04-3.01, in compliance with the requirements of commercial cast iron. The use of a solid fuel like coke, which is much more reactive at higher temperatures ($>1000^\circ C$) favors the reduction, contrary to lignite, which is much more reactive and evolves its thermal energy at lower temperatures.

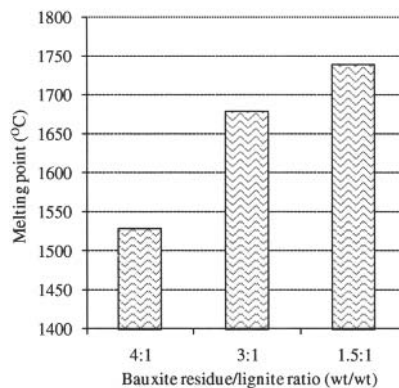


Figure 3. Effect of the ratio bauxite residue/lignite on the melting point

Table II. Experimental Conditions of Reduction Smelting Experiments and Chemical Analysis of the Metallic Product

Raw Material	Smelting s/n	Reducing Agent	BR/ Reducing Agent Ratio	Fluxes		Retention Time (min)	(% Content in the Metal)			
				SiO ₂ (g)	CaO (g)		Fe	S	C	Rest Admixtures
Pellets										
B.R. *	1	Lignite	4/1	-	-	15	94.8	0.1	3.4	1.7
B.R.	2	Lignite	4/1	35	5	15	91.3	0.7	5.4	2.6
B.R.	3	Coke	11/1	-	-	15	94.2	0.2	4.6	1.0
B.R.	4	Lignite	4/1	20	-	15	91.7	0.4	5.3	2.6
B.R.	5	Lignite	4/1	62	38	15	91.9	0.4	5.2	2.5
B.R.	6	Lignite	4/1	-	-	30	94.5	0.3	3.5	1.7
B.R.	7	Lignite	4/1	-	-	45	95.3	0.2	3.0	1.5
B.R.	8	Coke	11/1	-	-	30	95.0	0.1	3.2	1.6
B.R.	9	Coke	11/1	-	-	45	95.8	0.5	2.4	1.2
B.R.	10	Lignite	3/1	-	-	15	95.6	0.3	2.7	1.3
B.R.	11	Lignite	1.5/1	-	-	15	95.8	0.4	2.8	1.0

* BR: Bauxite Residue

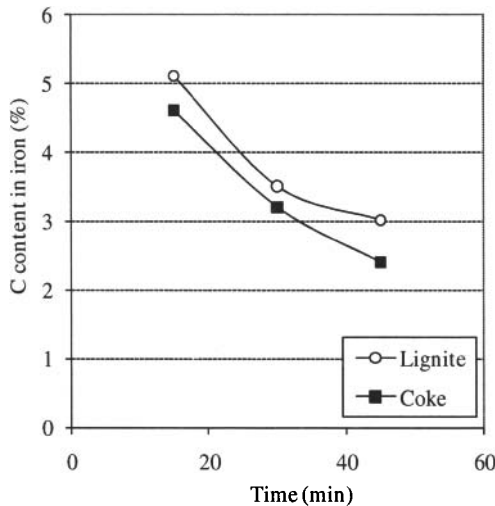


Figure 4. Effect of the reducing agent and retention time on carbon content of the metallic product (reducing agent in 50% excess of the stoichiometrically required quantity)

The addition of fluxes results in the alteration of the basicity index of the slag. The basicity index is determined within the framework of the current study as the ratio (bases/acids). The oxides FeO, MgO and CaO are considered as bases while SiO₂ is considered as acid. Al₂O₃ is considered as an amphoteric oxide, which means that an Al₂O₃ (%) content higher than 18% is considered as basic, and lower than 15% is considered as acidic. On the contrary, for Al₂O₃ (%) content 15-18, it does not participate in the slag basicity calculations.

More precisely, the addition of fluxes results in the alteration of the basicity index of the slag from 4.5 to 0.6, at an addition rate of 35 g SiO₂ and 5 g CaO per 100 g of bauxite residue/lignite mixture (Figure 5). Due to the reduction of slag basicity, the (%) sulfur content in the metallic product increases to approximately 0.7%. It is noted that the sulfur content of a typical cast iron should not exceed 0.04% and this constitutes a crucial parameter of its quality.

The addition of fluxes in the current work can be characterized as successful, since the melting temperature value measured by the optical pyrometer during the three experiments conducted with the addition of CaO and SiO₂, fluctuated between 1400-

1450°C. On the contrary, the melting temperature value measured the same way of the mixture of bauxite residue/lignite (4/1 by weight) was 1560°C. The aforementioned values are in agreement with the theoretically calculated melting temperature values from the ternary phase diagrams in Figures 6 and 7.

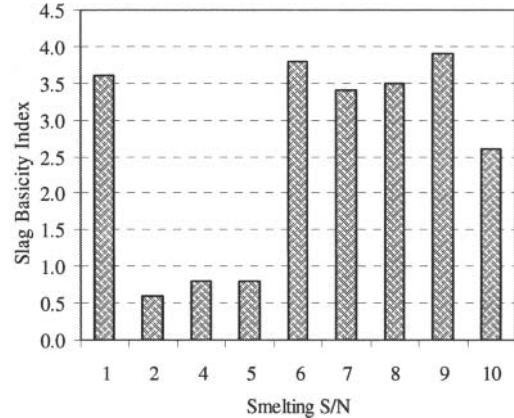


Figure 5. Basicity index of the slag samples produced

Moreover, the slag produced by the addition of 35 g SiO₂ and 5 g CaO (Point B) per 100 g of mixture (bauxite residue/lignite), is in the eutectic region of the slag produced by the blast furnace operation.

The smelting reduction of pellets of Greek bauxite residue with lignite (diameter of pellet: -9.5+6.3 mm, bauxite residue /lignite: 4/1 by weight) resulted in the production of a metallic product of good quality (94.8% iron and 3.1% carbon), something which is ascribed to the better contact of the bauxite residue with the solid reducing agent, favoring in such a way, the iron oxide reduction. This constitutes an essential conclusion taking into consideration that pelletization is a very common agglomeration process used in the iron ore industry.

A metallographical section of grains of the metallic product as well as the slag samples from the smelting reduction of bauxite residue with lignite (4/1 by weight) with the addition of 35 g SiO₂ and 5 g CaO per 100 g of the mixture, was studied by SEM/EDS (JEOL® JSM-6380LV). Back-scattered electron image of the aforementioned samples, are presented in Figures 8 and 9.

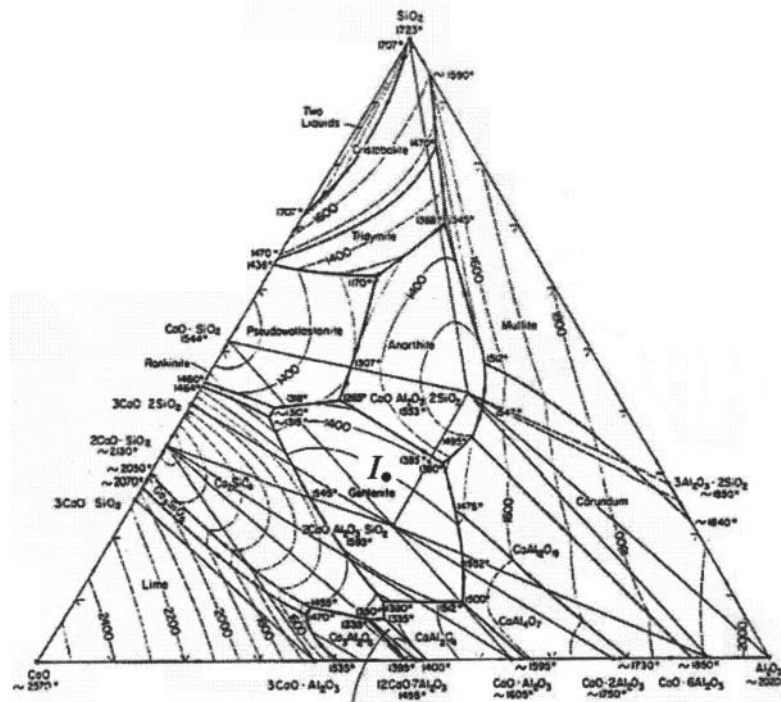


Figure 6. Melting temperature value of the slag sample produced by the mixture bauxite residue /lignite (4/1 by weight)

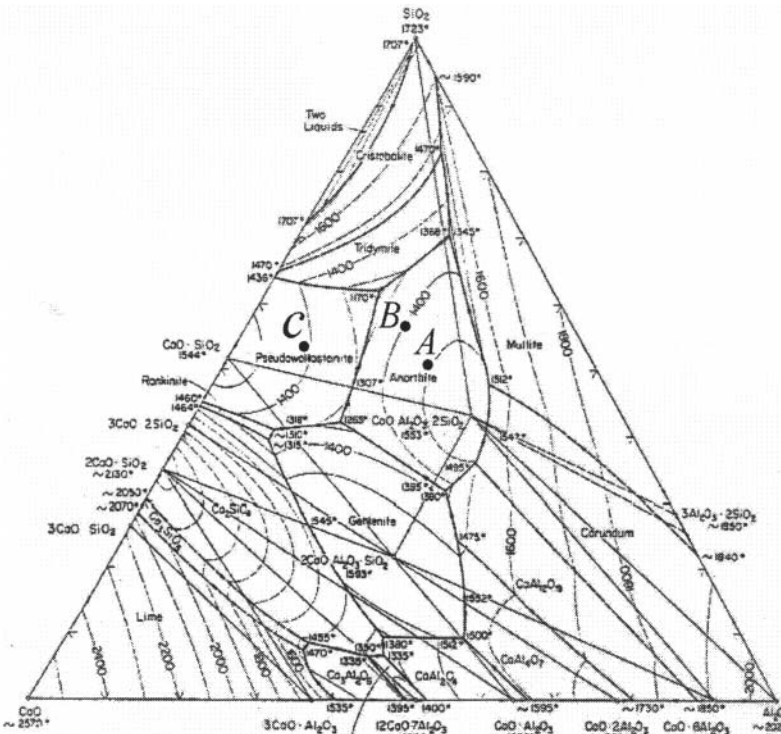


Figure 7: Melting temperature values of the slag samples (A,B,C) produced by the addition of: A) SiO₂-CaO: 20-0 g, B) SiO₂-CaO: 35-5 g, C) SiO₂-CaO: 62-38 g per 100 g of the mixture bauxite residue /lignite (4/1 by weight)..

Figure 8 shows a typical feature, where the metal matrix and the lamellar structure of iron carbide flakes can be seen. In Figure 9 a typical matrix of an iron ore slag is seen, where the black area corresponds to the slag oxides as determined by the EDS analysis. We have also focused on metal grain 'trapped' in the slag (white area), which is probably ascribed to the intense eddying of the molten bath due to the Foucault current, resulting in non satisfactory phase segregation (metallic product - slag).

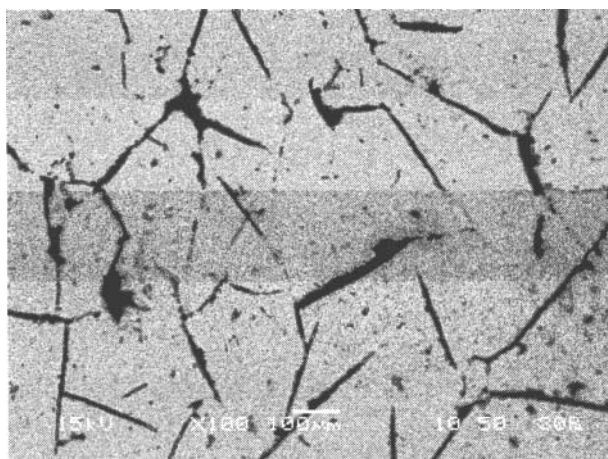


Figure 8. Back-scattered electron image of the metallic product from the smelting reduction of Greek bauxite residue with lignite.

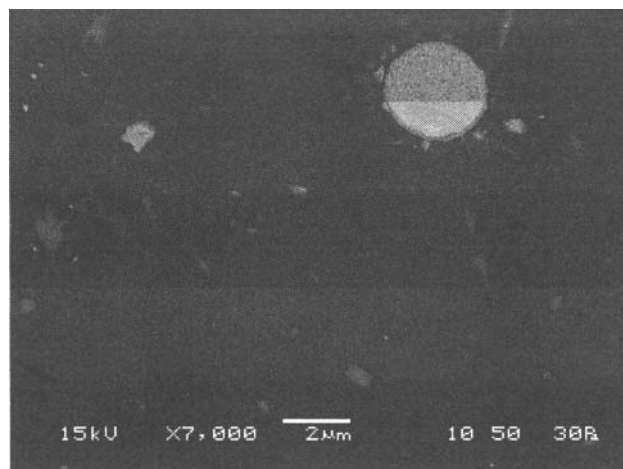


Figure 9. Back-scattered electron image of the slag phase from the smelting reduction of Greek bauxite residue with lignite.

Conclusions

Smelting reduction of Greek bauxite residue revealed that it can be used successfully for direct cast iron production. The

reduction smelting with solid reducing agents resulted in the production of a metallic product with an iron content fluctuating between 91-95.8%, which can be characterized as satisfactory considering that a typical cast iron has an approximate analysis of 91-96 % in iron. The addition of solid reducing agents results in a significant increase of the melting point of the bauxite residue, from 1400°C up to 1740°C for a great excess of the reducing agent, due to the formation of the refractory iron carbides. The addition of CaO and SiO₂ reagents as fluxes favored the decrease of the melting point, in agreement with the respective ternary phase diagrams. The type of the solid reducing agent used, proved to be a critical parameter affecting the quality of the metallic product, in terms of the desired sulfur content, the basicity of the slag and the kinetics of the reductive procedure. The results render the future investigation for optimization of the proposed processing method very promising. Apart from optimization of the iron recovery, intensification of the future research is necessary concerning the extraction of impurities, such as S, P and Ti from the metallic product.

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