

PHYSICAL METHODS AND INSTRUMENTATION

STUDY OF TRANSFER EFFICIENCIES OF MINOR ELEMENTS
DURING STEELMAKING BY NEUTRON ACTIVATION
TECHNIQUE

ANTOANETA ENE¹, ION V. POPESCU^{2,3,4}, VALENTIN GHISA⁵

¹“Dunărea de Jos” University of Galați, Domneasca 111, 800201 Galați, Romania, aene@ugal.ro

²“Valahia” University of Târgoviște, 2 Carol I street, 130024, Târgoviște, Romania,
ivpopes@valahia.ro

³“Horia Hulubei” National Institute for Physics and Nuclear Engineering,
Bucharest-Magurele, Romania

⁴ Science Academy of Romania,

(Received July 22, 2008)

Abstract. Neutron activation analysis was applied to investigate the behaviour of some metallurgical materials (pig iron, scrap, lime, LD steel, refining slag, sludge, ferroalloys, aluminum, coke, deoxidized steel, final slag) involved in the steelmaking process in LD converter in the Iron and Steel Works at Galati (Romania). The purpose of this work was to determine the transfer efficiencies of some minor and trace elements (Mn, Al, V, Cu, As, W) from the converter charge to the metallic bath during the two stages of the steelmaking process: refining and deoxidation.

Key words: minor elements, transfer efficiency, steelmaking, neutron activation technique.

1. INTRODUCTION

Knowledge of the chemical composition of raw and auxiliary materials involved in iron and steelmaking is important for the ferrous metallurgy and accurate methods of analysis must be used for this purpose. Trace and minor elements existing in the raw and intermediate materials can remain in iron and steel as residual elements (some of them being beneficial and others not) and influence their properties, a well known fact [1]. Among the methods used for such analyses, both thermal [2, 3] and 14 MeV [4] neutron activation was applied for the determination of minor elements in steel [2] and traces in iron ores [3] and ferroalloys [4]. In a previous paper we have applied thermal neutron activation analysis (NAA) for the determination of the compositional scheme of different metallurgical materials [5]. The purpose of this work was to determine the transfer efficiencies of some minor and trace elements (Mn, Al, V, As, W, Cu) from the

charge (pig iron, scrap, lime, ferroalloys, aluminum, coke) to the related final products (LD steel, refining slag, sludge, deoxidized steel, final slag) during the two stages of the steelmaking process in LD (Linz-Donowitz) converter: refining and deoxidation. Refining of the steel bath in this type of converter is accomplished by the injection of oxygen [6] which results in the oxidation of various elements; the order in which the reactions for the different elements occur depends on the concentrations, the bath temperature and the relative free energy value, ΔG^0 , for the respective elements [7]. The main raw materials for the basic oxygen process are hot metal (pig iron) from the blast furnace and scrap. Lime is used as flux which contributes to the separation of the slag from the steel. Deoxidation is applied in order to prevent the forming of the non-metallic inclusions as a result of the oxygen content increasing at the end of the refining [8]. The traditional method of deoxidation is to add elements with a higher affinity for oxygen than iron to the liquid steel. The most commonly used deoxidants, in increasing order of deoxidizing power, are ferromanganese, coke, ferrosilicon, ferrotitanium and aluminum [6].

2. EXPERIMENTAL

NAA was applied to a set of metallurgical samples (pig iron, scrap, lime, LD steel, refining slag, sludge, ferroalloys, aluminum, coke, deoxidized steel, final slag) involved in steelmaking process in the Iron and Steel Works at Galati (Romania). All the samples were taken from the same converter charge whose balance of materials is given in Table 1.

For a quantitative determination of elements the samples were simultaneously irradiated together with appropriate multielemental standards which had a similar matrix elemental composition and form of presentation such as British Chemical Standard No. 320, 420-1, 220-2, 173-1, Eurostandard No. 482-1, Euronorm CRM No. 085-1. In this way, variations due to γ - ray and neutron attenuation effects were minimized.

The samples and standards were carefully weighed into small polyethylene vials which, in turn, were enclosed in another polyethylene vial for irradiation. They were irradiated as massive pieces (with the exception of sludge) in the rabbit system of the VVR-S Nuclear Reactor of the Institute of Physics and Nuclear Engineering in Bucharest-Magurele, at a neutron flux of $10^{12} \text{ n}\cdot\text{cm}^{-2} \text{ s}^{-1}$ for a period of 15 s for short-lived nuclides and 30 m for long – lived nuclides. The cooling times of the short – lived nuclides were 2-8 m for Al and V and 2 h for Mn. For the long – lived nuclides countings were carried out at different decay times, ranging from 1 to 4 days, in order to best detect radionuclides of various half lives. The counting system for the measurement of the induced radioactivity in the samples and standards consisted of a Ge(Li) ORTEC detector with an appropriate electronic amplification system and a PC. The energy resolution of the system was 2.3 keV at 1.33 MeV.

Table 1
The balance of materials involved in the steelmaking process

a. REFINING		b. DEOXIDATION	
INPUT		INPUT	
Material	Quantity (t)	Material	Quantity (t)
LD steel (LD)	170	Pig iron (PI)	160
Refining slag (RS)	3.5	Scrap (SC)	25
Ferromanganese (FM)	3	Lime (L)	16
Ferrosilicon (FSI)	0.7	Oxygen (O)	13.2
Ferrotitanium (FT)	0.33	TOTAL INPUT (T.I.)	214.2
Aluminum (AL)	0.35	OUTPUT	
Coke (C)	0.07	Final product	Quantity (t)
TOTAL INPUT (T.I.)	177.95	LD steel (LD)	170
OUTPUT		Refining slag (RS)	25.1
Final product	Quantity (t)	Sludge (SG)	1.9
Deoxidized steel (DS)	173.6	Exit gas (G)	17.1
Final slag (FS)	4.3	TOTAL OUTPUT (T.O.)	214.1
TOTAL OUTPUT (T.O.)	177.9		

3. RESULTS

The elements determined in the iron and steel samples were the following: Mn, Al, V, As, W and Cu. Only a qualitative analysis was made for Ca, Na, K, Sb, La, Sm, Sc and Cr. The concentrations of the elements of interest are given in Table 2 and they are indicated in parts per million [ppm] or [%]. The statistical error of counting does not exceed 5%. Taking into account the data from Tables 1 and 2 we performed the balances of Mn, Al, V, As, Cu and W for the two stages of the steelmaking process, refining and deoxidation, which are presented in Tables 3 and 4, respectively. Using the data from Tables 3 and 4 we calculated the transfer efficiencies of Mn, Al, V, As, Cu and W in steel, slag and sludge from the expression:

$$\eta = \frac{E_i}{\langle E \rangle} 100, \quad E_i = \{ [E], (E), \{E\} \},$$

where η is the transfer efficiency of element E; $\langle E \rangle$, $[E]$, (E) and $\{E\}$ are the quantities of element E in the charge, steel (LD or deoxidized steel), slag (refining or final slag) and sludge respectively; results are given in Table 5.

Table 2

The concentrations of elements in iron and steel materials involved in the steelmaking process

Sample	Mn (%)	Al (ppm)	V (ppm)	As (ppm)	Cu (ppm)	W (ppm)
PI	1.02	280	85	240	626	4.8
SC	0.33	200	8	53	340	2.9
L	63 ppm	883	6	0,6	70	2
LD	0.12	200	17	220	630	4.6
RS	5.97	1160	436	1	95	3.5
SG	0.50	218	9	24	100	1.1
FM	63	5000	200	34	500	25
FSI	0.20	2.8 %	97	7	1147	64
FT	0.57	12 %	2080	-	-	-
AL	0.30	82 %	300	1	40	105
C	14 ppm	2300	347	0.2	70	1
DS	1.21	1050	25	216	630	5.4
FS	4.80	5 %	355	0.5	77	3

Table 3

The balance of manganese, aluminum, vanadium, arsenic, copper and tungsten for the refining (R) process

R	Mn (kg)	Al (kg)	V (kg)	As (g)	Cu (kg)	W (g)
PI	1632	44.8	13.6	38400	100.2	768
SC	82.5	5	0.2	1325	8.5	72.5
L	1	14.1	0.1	10	1.1	32
T.I.	1715.5	63.9	13.9	39735	109.8	872.5
LD	204	34	2.9	37400	107.2	782
RS	1498.5	29.1	10.9	25	2.4	87.8
SG	9.5	0.4	0.02	46	0.2	2.1
T.O.	1712	63.5	13.8	37471	109.8	871.9

Table 4

The balance of manganese, aluminum, vanadium, arsenic, copper and tungsten for the deoxidation (D) process

D	Mn (kg)	Al (kg)	V (kg)	As (g)	Cu (kg)	W (g)
LD	204	34	2.9	37400	107.2	782
RS	208.9	4.1	1.5	3.5	0.3	12.2
FM	1890	15	0.6	102	1.5	75
FSI	1.4	19.6	0.07	4.9	0.8	44.8
FT	1.9	39.6	0.7	-	-	-
AL	1	287	0.1	0.3	0.01	36.8
C	0.001	0.2	0.02	0	0.005	0.07
T.I.	2307.2	399.5	5.9	37511	109.8	950.9
DS	2100	182.2	4.3	37498	109.3	937.4
FS	206.4	215	1.5	2.1	0.3	12.9
T.O.	2306.4	397.2	5.8	37500	109.6	950.3

Table 5

Transfer efficiencies of manganese, aluminum, vanadium, arsenic, copper and tungsten in final products (FP) – steel, slag and sludge – during refining and deoxidation

FP	Transfer efficiency, η (%)					
	Mn	Al	V	As	Cu	W
LD	11.9	53.2	20.8	94.12	97.6	89.6
RS	87.3	45.5	78.7	0.06	2.2	10.1
SG	0.5	0.6	0.1	0.11	0.2	0.2
DS	91.0	45.6	72.9	99.96	99.5	98.6
FS	8.9	53.8	25.4	0.005	0.3	1.4

The elements taken into consideration may be divided after the chemical affinity for oxygen (oxygen potential of their oxides) in two groups [5] :

- i) elements with greater chemical affinity for oxygen (smaller oxygen potential) than that of iron (Mn, V, Al);
- ii) elements with smaller chemical affinity for oxygen (greater oxygen potential) than that of iron (Cu, As, W).

The behaviour of each group of elements is dictated by the prevailing chemical characteristic of the elaboration process.

In the case of the refining, which is an oxidation process, the elements with greater chemical affinity for oxygen than that of iron are oxidized and their oxides are eliminated as slagging oxides, gases or vapours. In the impact zone of the oxygen jet with the metallic bath, a local temperature of about 3000 °C is created and boiling points of the bath constituent elements are reached resulting in a vaporization of a small part (0.6–1.2 %) of the metallic charge. The vapours of Fe, Mn, Al, V, As etc. and the fine particles of flux are trained by the CO bubbles resulted from the bath decarburization and form the sludge.

4. DISCUSSION

Analysing the data from Tables 3-5 some conclusions can be drawn. During refining the manganese and the vanadium, because of their great chemical affinity for oxygen compared to that of iron, pass from pig iron and scrap to slag in large proportions: 87% for Mn and 79% for V; their transfer efficiencies in LD steel have small values: Mn – 12% and V – 21% (Table 4).

The aluminum passes only in a proportion of 45% into refining slag because it has a smaller chemical affinity for oxygen than manganese and vanadium. The transfer efficiency of aluminum in LD steel is 53% (Table 5).

Arsenic and copper are undesirable elements in steel [6]. They are present in pig iron in large quantities (Table 3) and have great transfer efficiencies in LD steel (> 94%) because of their smaller chemical affinity for oxygen than that of iron (Table 5). There is a difference between the input and output total quantities of arsenic (Tables 3 and 4); this arsenic loss is achieved by the volatilization in exit gas as As_2O_3 .

Tungsten, which is a beneficial element in steel, also has a great transfer efficiency (89%) in LD steel because of its smaller chemical affinity for oxygen than that of iron (but greater than that of arsenic and copper). Its presence in slag in a proportion of 10% is due to the formation of very stable compounds, such as calcium tungstates (Table 5).

Very small proportions (0.1–0.6%) of each element pass into sludge during refining.

During the deoxidation process the quantities of manganese and aluminum in the bath increase because of the addition of the deoxidants – ferromanganese and aluminum – which contain these elements as major constituents (Table 4). The transfer efficiencies of Mn, V and Al in the deoxidized steel are 91%, 73% and 45% respectively.

Arsenic and copper remain in a high proportion (99%) in the final product – the deoxidized steel.

The quantity of tungsten in the bath increases because its presence in the used ferroalloys and aluminum (Table 4). This element is almost entirely recoverable toward the end of the deoxidation process [7] having a transfer efficiency of 98% in the deoxidized steel.

5. CONCLUSIONS

Knowing the transfer efficiencies of the residual elements in LD steel, the steelmaking process can be conducted so that the recuperation of the elements with favorable influence upon steel characteristics (Mn, Al, V, W) should be accomplished. As regards the undesirable elements for steel (As, Cu), they are transferred from pig iron and scrap to LD steel and further to deoxidized steel. Taking into account the fact that these elements pass from iron ores to pig iron [6] it is very important to choose the appropriate proportions of iron ores which contain these elements in high concentrations.

REFERENCES

1. Yu.S. Yusfin, P.I. Chernousov, V.I. Solodkov, Yu.A. Karpov, A.L. Peletin, S.V. Nedelin, *Metallurgist*, **43**, 211 (1999).
2. J. Hoste, F. Bouten, F. Adams, *Nucleonics*, **19**, 118 (1961).
3. M. A. Raouf, A. Naeem, R. Zaghoul, A. F. Abdul-Fattah, M. A. Obeid, *J. Radioanal. Chem.*, **60**, 273 (1980).
4. A. M. El-Khatib, S. A. Mahmoud, B. M. Moharram, *Isotopenpraxis*, **22**, 239 (1986).
5. I. Popescu, T. Badica, A. Olariu, C. Besliu, A. Ene, Al. Ivanescu, *J. Radioanal. Nucl. Chem., Letters*, **213**, 369 (1996).
6. R. W. Cahn, P. Haasen, E. J. Kramer, *Materials Science and Technology. A Comprehensive Treatment, Vol. 7: Constitution and Properties of Steels*, VCH, Weinheim, New York, Basel, Cambridge, 1992, pp. 95–145.
7. C. Bodsworth, H. B. Bell, *Physical Chemistry of Iron and Steel Manufacture*, Longman, London, 1972.
8. R. Kiessling, N. Lang, *Non-metallic Inclusions in Steel*, The Metals Society, London, 1978.