RECOVERY OF VANADIUM FROM V-BEARING BOF-SLAG USING AN EAF

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ABSTRACT

Experiments on a vanadium recovery method from vanadium containing BOF-slag using a 10 tons electric arc furnace (EAF) were conducted. The aim was not only to recover vanadium efficiently but also to make the treated BOF-slag useful for external markets. The vanadium and other valuable metals were extracted into a metal phase by pre-reduction using carbon-based reductants and final-reduction by injection of ferrosilicon- and/or aluminium powder.

The results did show that in excess of 98% of vanadium could be recovered to the metal by this method, most of the iron and phosphorus was also successfully recovered to the metal. The reduced BOF-slag has a vanadium-content as low as 0.02mass% and thus has good opportunity to be used as construction material. The tested parameters important for the process are described and discussed in details in this paper.

1 INTRODUCTION

Today, about 50% of the BOF-slag at SSAB in Sweden is recycled to the blast furnace and the rest is temporarily stored inside the steel plant. The BOF-slag can not be used externally due to its content of vanadium and free lime. As the slag storage area is limited this has become a problem for SSAB. The disposition of the slag is also a great waste of vanadium resource. The current potential value of vanadium in the discharged BOF-slag annually amounts to roughly US$ 100 millions.

Various attempts have been made in Sweden to recover vanadium from the BOF-slag. In one of the most recent projects a method called IPBM (In-Plant By Product Melting) for carbothermal reduction of BOF-slag using a DC-furnace with hollow electrode was developed at Swerea MEFOS [1]. The aim of the project was to remove vanadium from the slag and make it useable outside the steel plant. The ferroalloy obtained from the slag reduction contained about 10mass%V, 5-6mass%Mn and 1mass%P, corresponding to a vanadium recovery of more than 90%. The vanadium content of the residual slag was in general between 0.5-1mass%. According to Swedish conditions it is expected that for use of the reduced slag in the cement industry and for road construction the vanadium content in the slag should be lower than 0.1mass% and 0.3mass% respectively.

The present study aims at the development of a method not only to recover vanadium efficiently but also to make the reduced BOF-slag useful for external markets. The present method is based on pre-reduction using carbon and final-reduction using ferrosilicon and/or aluminium powder for treatment of hot BOF-slag. By using hot BOF-slag taken directly from the converter more than half of the energy needed for treatment of the slag can be saved compared with treatment of cold slag. The experiments were carried out in the end of 2008 using a 5 MVA electric furnace at Swerea MEFOS.

2 EXPERIMENTAL SETUP

2.1 Materials

The composition of the treated BOF-slag with high vanadium content and the used slag formers, sand and bauxite, are shown in Table 1 and the reductants in Table 2 below.

Table 1: Chemical composition of the oxide materials used in the pilot campaign. Particle size of BOF-slag and sand was -6+2mm and for Bauxite -5+3mm.

	Stable oxides (mass%)				Less-stable oxides to be reduced (mass%)						
	Al_2O_3	CaO	MgO	SiO_2	Cr_2O_3	FeO	Fe_2O_3	MnO	P_2O_5	TiO_2	V_2O_5
BOF	2.20	41.95	8.93	9.31	0.20	22.40		3.55	0.55	1.82	4.35
Sand	0.68	0.03	0.17	98.5		0.23		0.01	0.01	0.02	
Bauxite	88.10	0.16		5.57			1.42			3.56	

Table 2: Composition and particle size of anthracite, pulverized coal and graphite used for pre-reduction and ferrosilicon and aluminium that was used for final-reduction of BOF-slag.

Reductant	Composition	Particle size
Anthracite	C-fix 91mass%	-6mm
Pulverized coal (PCI)	81mass% C	Powder
Pulverized graphite	99mass% C	Powder
Ferrosilicon	75mass% Si	-2mm
Aluminium granulates	98mass% Al	-3.5+1mm

2.2 Experimental setup and procedures

One test campaign for three days was carried out at Swerea MEFOS, using a 5 MVA AC furnace with MgO based lining as the basic equipment for BOF-slag reduction. A schematically drawing of the experimental setup is shown in Figure 1.

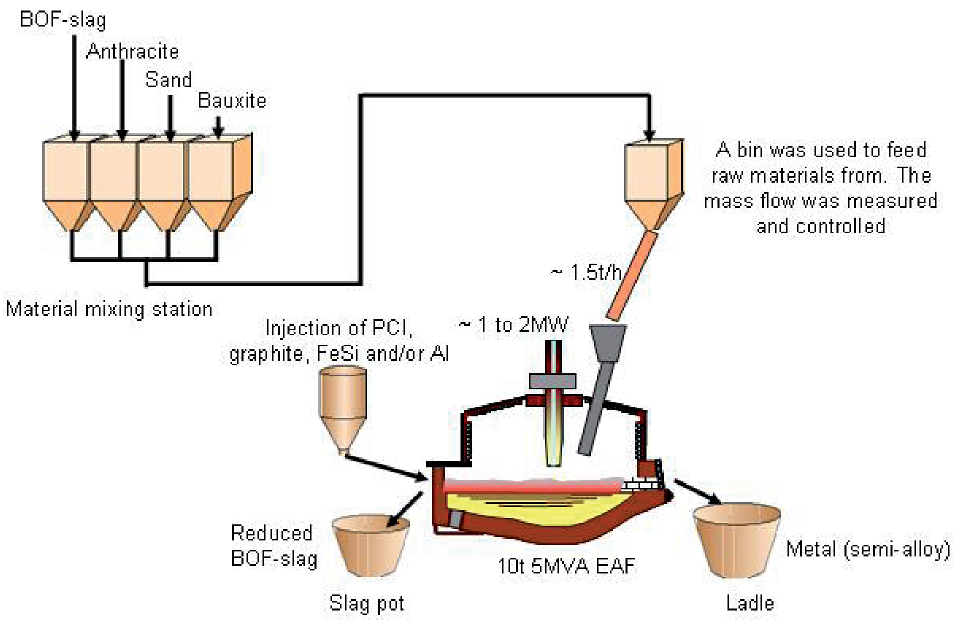

Figure 1: Schematically drawing of the experimental setup using a 5 MVA AC furnace with MgO based lining as the basic equipment for BOF-slag reduction.

All tests started with a metal bath of about 5 tons (~0.2mass% C). The continuous feeding of the pre-mixed material containing the BOF-slag to be treated on the 5t metal bath was carried out via a chute positioned in the middle of the three electrodes. Slag formers were chosen aiming for a liquid slag at a process temperature of 1650°C. The method is based on pre-reduction using carbon based reductants and final-reduction using ferrosilicon and/or aluminium powder. During reduction of BOF-slag, chromium, iron, phosphorous, manganese and vanadium will be reduced into the metal phase. Slag skimming through the slag door into a slag pot was carried out between each test; the metal was tapped into a ladle in the end of each day. In this way, there will be a build-up of the reduced elements in the metal bath over the processing time.

Two main methods for pre-reduction were tested:

- Pre-reduction by pre-mixing BOF-slag and anthracite.
- Injection of pulverized coal and graphite in the molten slag (to simulate treatment of hot BOF-slag).

Two main methods for final-reduction were also applied:

- Injection of ferrosilicon and/or aluminium in the molten slag.
- Injection of an excess amount of ferrosilicon in the metal, after slag skimming the metal was poured through the slag.

Process data such as power input, gas analysis, feeding rate, specific energy consumption (MWh/t) etc. were recorded second by second. Metal samples were collected from the liquid metal using a standard sampling probe. The slag samples were taken with a slag spoon and quenched in air. The analysis method used for both metal- and slag samples were X-ray fluorescence spectroscopy.

3 RESULTS AND TECHNICAL EVALUATION

Totally 13 tons of BOF-slag with high vanadium content was treated in 13 trials. Various process parameters such as reducing agents, energy consumption and slag basicity were investigated. The process temperature was controlled by adjusting the power input (~1-2 MW) and keeping the feeding rate of BOF-slag constant. The main results are shown in Tables 3 and 4.

The final metal analysis in each test is shown in Table 4 below, as shown in the table the V-content in the hot metal increased gradually with time, in an industrial process a hot metal with about 10% V is expected.

Table 3: The energy consumption per ton BOF-slag during melting of the pre-mixed material, the final slag analysis and the vanadium yield.

Test	MWh/t	Final slag analysis (mass%)									V-y.
ID	BOF-sl.	Fe	V	CaO	SiO_2	MnO	P_2O_5	Al_2O_3	MgO	Cr_2O_3	(%)
1	1.7	0.06	0.02	41.69	20.46	0.13	0.02	26.52	15.16	0.01	99.3
2	1.2	0.11	0.06	41.97	20.72	0.21	0.02	28.21	13.24	0.02	98.0
3	1.2	1.71	0.17	40.18	24.34	1.03	0.02	18.99	14.43	0.04	94.3
4	1.7	0.29	0.29	41.63	32.77	1.23	0.01	9.48	14.72	0.02	90.6
5	1.4	1.28	0.22	38.67	34.14	1.35	0.02	9.73	15.01	0.02	92.8
6	1.1	0.19	0.05	36.64	34.83	0.72	0.01	10.85	17.14	0.02	98.3
7	1.5	0.07	0.03	37.62	14.17	0.21	0.01	37.92	11.22	0.01	99.1
8	1.3	0.64	0.04	37.20	23.53	0.34	0.01	27.86	11.92	0.01	98.7
9	1.4	0.41	0.28	35.79	24.48	1.19	0.00	24.68	14.23	0.01	90.8
10	1.6	0.94	0.51	33.29	32.17	1.92	0.01	5.36	14.16	0.02	83.3
11	1.3	0.15	0.08	35.88	40.62	0.84	0.00	4.93	20.79	0.02	97.2
12	1.6	0.10	0.05	38.21	33.11	0.63	0.01	13.07	17.47	0.02	98.3
13	1.5	0.20	0.07	35.17	32.72	1.42	0.00	15.23	16.74	0.02	97.8

3.1 The reduction efficiency of the process

Most of the iron, phosphorus and vanadium have successfully been recovered in the metal phase. It is clearly shown by Table 3 that high reduction degree in terms of reduction of Fe-, Mn-, P- and V-oxides in the slag has been achieved. The P-recovery is 97-99%, the Mn-recovery 50-96% and the Fe-recovery is generally over 90%. This demonstrates the high reducing efficiency of the process concept.

Table 4: Final metal analysis, initial Si-content in the metal and the metal temperature.

Test	Final metal analysis (mass%)							Si_{Me} ini.	Temp
ID	C	S	Si	Mn	P	Cr	V	(mass%)	(K)
1	0.045	0.017	1.126	0.780	0.123	0.065	0.464	0.000	1978
2	1.210	0.007	1.017	1.050	0.181	0.094	0.789	1.126	1916
3	1.710	0.004	3.574	1.390	0.217	0.114	1.087	1.017	1877
4	0.226	0.014	0.126	0.470	0.056	0.046	0.149	0.000	1922
5[1]	0.685	0.013						0.126	1898
6	1.100	0.010	1.065	0.880	0.140	0.035	0.797	0.749	1899
7	1.440	0.007	2.100	1.450	0.181	0.114	1.104	1.065	1902
8	1.800	0.001	3.957	1.790	0.205	0.134	1.380	2.100	1948
9	0.181	0.008	0.220	0.230	0.033	0.025	0.055	0.000	1915
10	0.455	0.016	0.579	0.350	0.092	0.054	0.375	0.220	1968
11	0.689	0.013	1.059	0.720	0.134	0.083	0.774	0.576	1978
12	1.080	0.010	1.120	1.050	0.162	0.105	1.132	1.059	1965
13	1.260	0.010	0.554	1.080	0.206	0.126	1.432	1.120	1958

[1] Inhomogeneous sample (pores).

3.2 V-recovery

The recovery yield of vanadium could be expressed by the following equation:

$$y_V(\%) = \left(1 - \frac{\%V_{RS}}{\%V_{BOF}} \cdot \frac{W_{RS}}{W_{BOF}}\right) \cdot 100 \quad (1)$$

where $\%V_{RS}$, $\%V_{BOF}$, W_{RS} and W_{BOF} are the V-content in reduced slag, the V-content in BOF-slag, the amount of final slag and the amount of treated BOF-slag, respectively. The W_{RS}/W_{BOF}-ratio was put to 0.80 in all tests based on the overall material balance.

Figure 2 shows the V-yield as a function of the V-content in the reduced slag ($\%V_{RS}$). The maximum allowed V-content in the reduced slag for use in both road construction and in the cement industry according to Swedish conditions are also presented. The final vanadium content is lower than 0.3mass% in 12 out of 13 tests. Vanadium recovery yields over 99% have been obtained (numerical values are shown in Table 3 above).

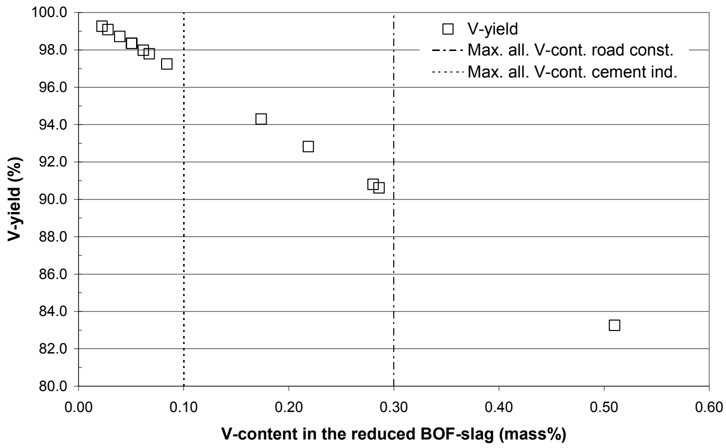

Figure 2: The V-yield as a function of the V-content in the final slag.

3.3 Energy efficiency

The energy consumption during melting of the pre-mixed material varied between 1.1 to 1.7MWh/t BOF-slag including heat losses, depending on the amount of anthracite in the pre-mixed material and the initial amount of dissolved silicon in the metal. The furnace power during final reduction was in general low due to the excess heat produced when Si and Al are oxidized to SiO_2 and Al_2O_3 respectively. The energy consumption was quite close to the theoretically estimated one if the heat losses are considered showing the high heat efficiency of the process.

3.4 The slag cleanness and quality

Vanadium contents down to 0.02 mass% in the slag have been achieved; thus the reduced slag has the potential to be used both in road construction and in the cement industry. The Cr-oxide content in the slag was reduced from 0.2mass% to 0.01-0.02mass% making it possible for external uses.

3.5 Effect of basicity

In Figure 3 the MgO- and the V-content in the slag at different slag basicities is presented. In the production of ferrovanadium by silicothermic (FeSi) reduction it has been reported that the vanadium recovery is less than in aluminothermic reduction and rarely exceeds 80%, the main reason is that VOx reacts with silica and forms vanadium silicates [2]. Nevertheless the results indicate that V-contents below the lower target value of 0.1mass% in the reduced slag could be obtained even when combining sand and ferrosilicon; however the lowest V-contents in the slag was found when using bauxite as slag former. There is also a tendency that the dissolution of MgO from the lining was higher when using sand compared to bauxite.

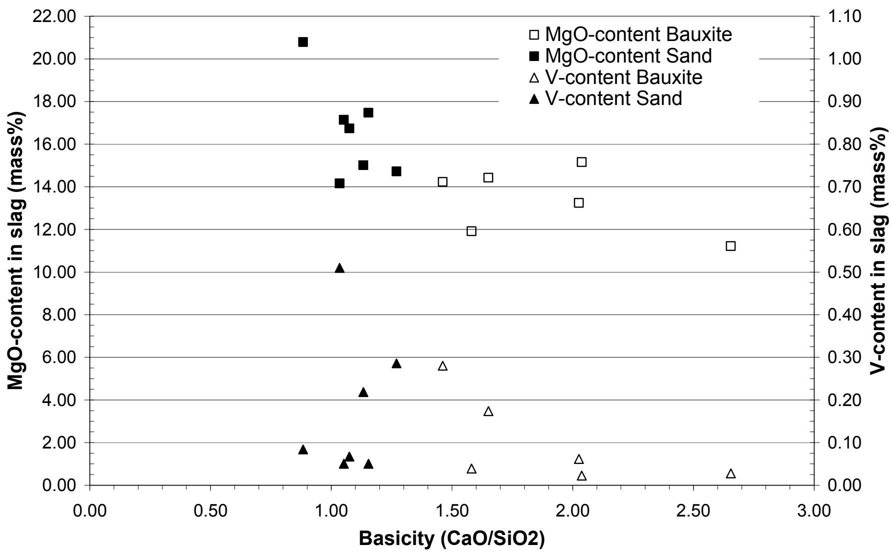

Figure 3: MgO-content in the slag as a function of slag basicity (CaO/SiO_2).

3.6 Silicon yield

The degree of reduction is to a large extent controlled by the Si-content in the metal bath. It is shown in Figure 4 that the V- and Fe-content is decreasing with increasing Si-content in the metal bath.
The yields of reductants closer to the stoichiometric amount can be expected in an industrial process by utilize the residual silicon and carbon in the metal.

Test 3 and 8 was an attempt to simulate this procedure by first injecting ferrosilicon into the metal phase and after slag skimming the metal was poured through the slag. This procedure had however no significant effect due to that the less-stable oxides had already been reduced to low levels.

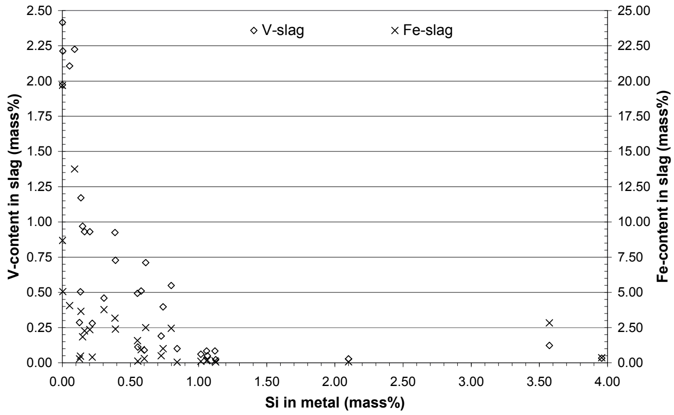

Figure 4: The V- and Fe-content in slag as a function of the Si-content in the metal.

3.7 Vanadium content in the slag during final reduction

Two main methods for final-reduction were applied:

- Injection of ferrosilicon and/or aluminium in the molten slag.
- Injection of an excess amount of ferrosilicon in the metal, after slag skimming the metal was poured through the slag.

The results is for sake of clarity divided in three parts, final reduction using FeSi, final reduction using Al and final reduction by using both FeSi and Al. For comparison test 8 and 11 is shown in Figure 5, injection of FeSi in the metal- and in the slag phase respectively. The results indicate that V-contents below the lower target value of 0.1mass% in the reduced slag could be obtained by using FeSi. The results also verify the earlier statement that the degree of reduction is to a large extent controlled by the Si-content in the metal bath; thus the time effect is of importance.

Trials with aluminum injection into the slag phase are shown in Figure 6. By comparing Figure 5 and 6 it can be concluded that the efficiently of ferrosilicon is almost in the same range as of the aluminium, despite that the initial V-content in the slag (after pre-reduction) is about 0.5 mass% higher in test 11 compared to test 12 and 13.

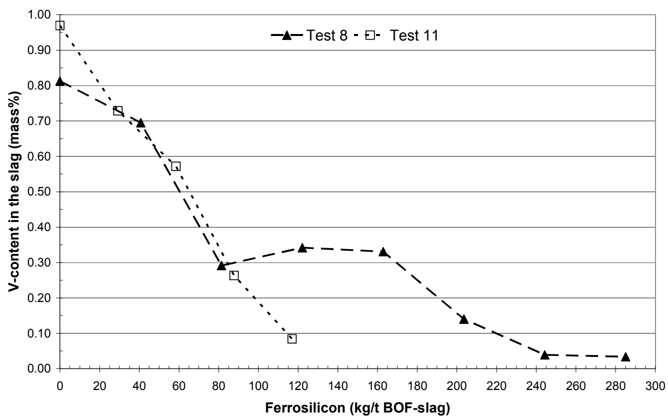

Figure 5: Final reduction by injection of FeSi in test 8 (into the metal phase) and in test 11 (into the slag phase).

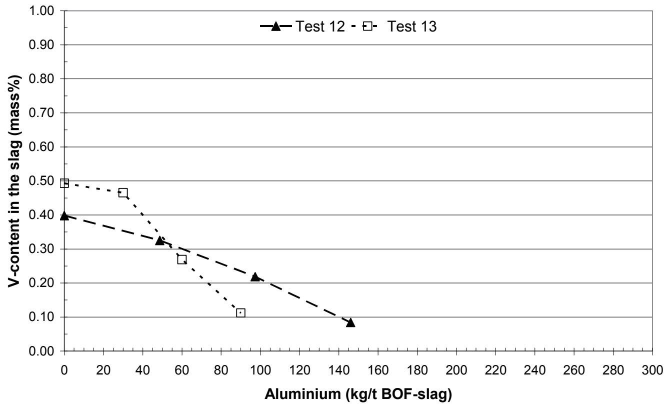

Figure 6: Final reduction by injection of Al in the slag in test 12 and 13.

In test 6 and 7 both FeSi and Al was used as reductants, shown in Figure 7. It clearly demonstrated that FeSi is sufficient effective to attain V-content of 0.1mass% or lower in the slag

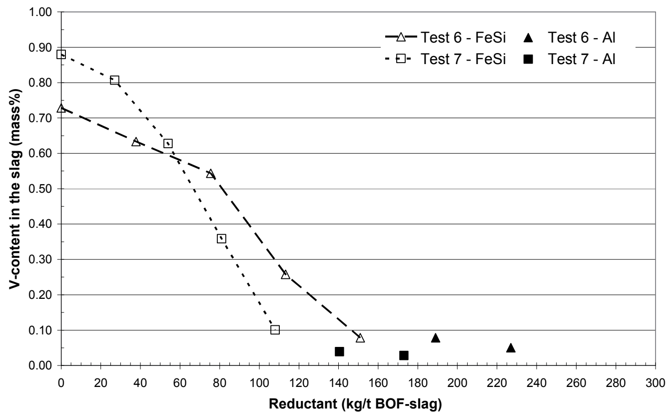

Figure 7: Final reduction by injection of both FeSi and Al in the slag in test 6 and 7.

4 CONCLUSIONS

It has been demonstrated in pilot scale that it is possible to recover more than 95% of vanadium in the SSAB BOF-slag using a two steps reduction procedure, starting with carbon reduction and finalizing by FeSi/Al reduction. The obtained reduced slag has a low V- and Cr-content which makes it possible for external uses.

5 REFERENCES

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