VANADIUM RECOVERY AS FeV FROM PETROLEUM FLY ASH

Y. Xiao[1], C. R. Mambote[2], H. Jalkanen[1], Y. Yang[1] and R. Boom[1]

[1] Department of Materials Science and Engineering, Delft University of Technology
Mekelweg 2, 2628 CD Delft, the Netherlands; y.xiao@tudelft.nl
[2] Consultek Research, Overhandstraat 2, 3195 SG Pernis Rotterdam, The Netherlands

ABSTRACT

Petroleum fly ash is a solid residue generated in the power plants using crude oil and petroleum coke as fuel, which is a valuable resource for vanadium. Stricter environmental regulations and sustainable material utilization demand high vanadium recovery, safer treatment and disposal. Several processes are reported in the literature for extracting vanadium from the fly ashes, such as roasting vanadium bearing materials in the presence of sodium salt, combined with alkaline or acidic leaching; or direct leaching the fly ash with sulphuric acid to produce vanadium pentoxide. The research efforts are mainly focused on selective leaching of the vanadium from ashes.

In the present study, lab-scale experiments have been conducted to recover vanadium from the ash for direct FeV production. The objective is to develop a sustainable processing technology, and further to minimize the environmental foot-print in the metallurgical industry. Two waste ash residues are used as raw materials for the process, and the reducing agent is also from the waste ash. The reaction stages are identified based on both the experimental results and the thermodynamic predictions. The thermal behaviour and distribution of various elements are investigated. It is intended to explore the feasibility of producing ferrovanadium based mainly on the waste resources, and to investigate the problems encountered and the process limitation.

1 INTRODUCTION

Vanadium, as a transition metal, has broad applications in various fields, especially as an alloying element in steelmaking. The driving force for vanadium production is largely dependent on the steelmaking industry. FeV is an intermediate alloy, important for the V-steel production. The annual vanadium production is approximately 60000 tons in 2008 [1] with about 5% yearly increase of the vanadium consumption due to the further development of the High strength low alloy steels [2]. The dominating countries for FeV production are China, South Africa, Russia, Australia and the United States [3]. Production of FeV is normally based on V_2O_3 or V_2O_5 using Al or FeSi as reductants. Iron scrap is usually first melted in an electric arc furnace, followed with a mixture of V_2O_5, Al and slagging flux [4, 5]. A considerable amount of FeV produced in Japan, USA and EU is based on processing petroleum residue and spent catalyst. These countries also import a large amount of V-slags from S. Africa, China and Russia for V_2O_5 and FeV production. For a comprehensive valorisation of the industrial waste resources, it would be more beneficial to develop a recipe based processing route of various waste streams. For example, to utilize the residue carbon in some waste material as the reductant for metal or alloy production. So far, no prior research is found in the literature in this combined waste processing technology for FeV production.

A power plant using petroleum fuels generates solid residues, which are collected in the off-gas treatment system as fly ash. The fly ash from burning petroleum oil is an important secondary resource for vanadium, after the primary resource of the ore concentrates and the metallurgical slag. According to the information in literature [6], hydrometallurgical processing is usually found as the preferred route for the recovery of vanadium from the fly ash, due to the relatively low operating and energy cost. The examples include alkali and acid leaching, or roasting then water/alkali/acid leaching followed by purification (solvent extraction or ion exchange) and V_2O_5 precipitation. As a high temperature processing route, an arc flash reactor was reported to process the fly ash using anthracite and petroleum coke as the reductant for producing ferronickel and ferrovanadium through

selective reduction [7]. Abdel-latif [8] reported an alternative flow sheet to recover vanadium from fly ash for ferrovanadium production: drying, de-carburization, de-sulphurization and smelting reduction with aluminum or ferrosilicon. In both of these studies [7, 8] steel scrap was used as the source of iron.

BOF steelmaking flue dust and sludge have been used or recycled with less than 50% on average [9]. Steelmaking flue dust contains quite high amount of iron oxides (up to 85% after drying), and with relatively low heavy metal contents depending on the quality of the scrap charge. Typically it is recycled within the steel plant in the sintering plant for the charge into the iron-making blast furnace. The critical issue is the heavy metal content such as Zn and Pb originating from the charged scrap in the BOF furnace. The flue dust can also be recycled back to the oxygen steelmaking converter, and the Zn and Pb will be accumulated in the flue dust. When the concentration of the heavy metals is high (e.g. >20 wt%), it can be used alternatively as a resource for heavy metal production (Zn and/or Pb). In general the major problem for the total recycling is the high zinc contents in the flue dust.

A more attractive approach of processing waste streams will relate to the demand of market oriented products and the motivating force of converting environmentally hazardous waste streams (flue dust, fly ash, or special slags) into products or intermediate products which are stabilized for utilization or disposal. The major component in the petroleum fly ash is $VOSO_4 \cdot 3H_2O$, which is considered as an important source of vanadium, instead of the traditional V_2O_5 used for FeV production. The high FeO_x and CaO contents in the BOF flue dust provide the necessary secondary resource for alloying and slag formation. The significant amount of carbon in the petroleum fly ash could serve as the reductant at least in the pre-reduction stage. A comprehensive recipe-based processing route needs to be developed for processing the waste stream from the metallurgical industry and to close the element cycle including the heavy metals.

In the present study, a preliminary investigation has been conducted to recover the metal values for FeV production from two industrial waste resources (fly ash and flue dust) with a pyro-metallurgical treatment. The mixture of the petroleum fly ash and BOF steelmaking flue dust is tested as the first case. The high temperature behavior of the fly ash and flue dust is investigated with a combined approach of chemical, thermal and off-gas analyses.

2 RAW MATERIALS CHARACTERIZATION

Petroleum fly ash and BOF flue dusts obtained from industrial operations were first dried and analyzed with LECO, XRF and XRD for elemental compositions and crystalline phase identification. Table 1 lists the compositions of the petroleum fly ash (BOO FA) and the BOF flue dusts (after drying at 105°C for 48 hours). The BOF steelmaking flue dust collected from a wet scrubber consists of a coarse fraction and a fine fraction (as received).

According to the XRD analysis, vanadium in the petroleum-fly ash occurs mainly in the form of $VOSO_4 \cdot 3H_2O$, and the existing form of nickel is identified as $NiS_2O_6.6H_2O$. There are significant amounts of carbon, and certain amounts of $MgSO_4 \cdot 6H_2O$ and $CaSO_4$. From the LECO analysis, the carbon content is 36.5 wt%, and sulphur content is 12.3 wt%.

The main crystalline phases identified with XRD for the BOF coarse fraction (BOF-CF) is found to be $Ca(OH)_2$, followed by $CaCO_3$, Fe_2O_3, FeO, and certain amounts of MgO. The BOF fine fraction (BOF-FF) contains similar components with significantly higher amounts of metallic iron and FeO and Fe_2O_3. The existing forms of heavy metals could not be identified due to the low concentrations.

The ash and flue dusts contain significant amounts of moisture and volatile matters. A drying test was conducted to determine the moisture content of the samples. Low temperature tests of loss on ignition (LOI) were carried out at 400°C for 2 hours in air to determine the low temperature volatiles. The results are listed in Table 2.

Table 1: Compositions of the petroleum fly ash and the BOF flue dusts with XRF and LECO analysis.

Element, wt%	Fe	V	Ni	Si	Ca	Al	Mg	S	P	Na	K
BOO FA-1	0.767	27.56	5.925	0.269	0.788	0.058	2.645	12.75	0.023	1.386	0.080
BOF-coarse	36.03	0.033	0.008	0.705	42.55	0.222	7.400	0.049	0.008	0.053	0.045
BOF-fine	82.95	0.026	0.000	0.740	8.535	0.043	1.247	0.053	0.050	0.203	0.033
Element, wt%	**Ti**	**Cr**	**Mn**	**Zn**	**Pb**	**Cu**	**Cd**	**Cl**	**C (LECO)**	**SUM**	**S (LECO)**
BOO FA-1	0.133	0.000	0.022	0.052	0.059	0.049	0.000	0.000	36.5	89.1	12.3
BOF-coarse	0.070	0.015	0.625	0.193	0.011	0.010	0.000	0.027	0.570	88.6	0.002
BOF-fine	0.024	0.028	1.429	0.370	0.065	0.000	0.012	0.012	1.650	97.5	0.039

Table 2: Ash drying and low temperature LOI tests

Properties	V-FA	BOF-CF	BOF-FF	Remarks
Moisture, %	10.1	16.4	24.4	at 105°C for 48 hours in air
LOI, %	22.8	2.03	-9.86	At 400°C for 2 hours in air

BOF flue dust is with high magnetic characteristics, and it is however very difficult to separate into magnetic and non-magnetic fractions due to the fine particle size. The moisture contents were determined to be 10.1 wt% for petroleum fly ash; 24.5 wt% for the BOF fine fraction flue dust; and 16.4 wt% for the BOF coarse fraction flue dust. When the dried ash samples were heated in air at 400 °C for two hours, there is a significant weight loss with petroleum fly ash of 22.8 wt%; and with 2.03 wt% for the BOF flue dust the coarse fraction. Due to the significant amount of metallic iron and wustite in the fine fraction of the BOF flue dust, there is about 10 wt% weight gain during heating in the air, because of the oxidation.

3 THEORETICAL EVALUATIONS

The initial inspiration of this study is the maximum use of the available components in the petroleum fly ash and BOF flue dust: the free carbon and the source of vanadium in the fly ash; the source of iron and the high lime content in the BOF flue dust. Addition of sand as a fluxing agent or FeSi as additional reducing agent can assist in the slag formation in the smelting reduction. The major chemical reactions within this designed system for FeV production can be written as follows:

a) Dehydration and sulphates decomposition of the petroleum fly ash: <1000 °C

$VOSO_4 \cdot 3H_2O = VO_2 + SO_2\,(g) + 0.5\,O_2\,(g) + 3\,H_2O\,(g)$ (1)
$NiSO_4 = NiO + SO_2\,(g) + 0.5\,O_2\,(g)$ (2)
$SO_3\,(g) = SO_2\,(g) + 0.5\,O_2\,(g)$ (3)

b) Solid-gas pre-reduction: 1000 – 1400 °C

$FeO + CO\,(g) = Fe + CO_2\,(g)$ (4)
$VO_2 + 2CO\,(g) = V + 2CO_2\,(g)$ (4a)
$NiO + CO\,(g) = Ni + CO_2\,(g)$ (4b)
$CO_2\,(g) + C\,(\text{residue in ash}) = 2CO\,(g)$ (5)

c) Smelting Reduction: >1400 °C (assuming ash melting and slag formation at 1400°C)

$(FeO) + CO\,(g) = Fe_{(l)} + CO_2\,(g)$ (6)
$VO_2 + 2CO\,(g) = [V]_{Fe} + 2CO_2(g)$ (6a)
$NiO + CO\,(g) = [Ni]_{Fe} + CO_2(g)$ (6b)
$CO_2\,(g) + [C] = 2CO\,(g)$ (7)

The reaction (1) is the total reaction taking place in several steps in the system including dehydration and decomposition of sulphate and SO_3. The temperature range is roughly estimated based on the reaction thermodynamics. Silica will be added into the mixture to bind lime and other oxides for slag formation. The advantage of using aluminium as the reductant is the high exothermic reaction. Lime in the BOF flue dust will promote the alumina (or silicate) slag formation, avoiding the usage of the slag

agent such as fluorspar. The high temperature thermodynamic stability of the major components in the ashes is evaluated with HSC chemistry software [10]. Figures 1 and 2 illustrate the thermodynamic calculation of the sulphates decomposition and the related oxides reduction with CO, as a prediction at the temperature range from room temperature to 1550°C.

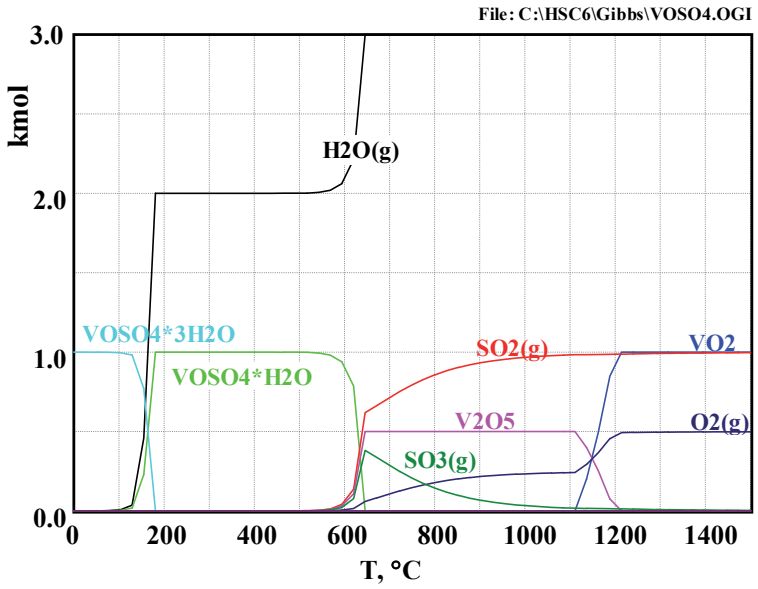

Figure 1: Equilibrium relations of $VOSO_4 \cdot 3H_2O$ decomposition

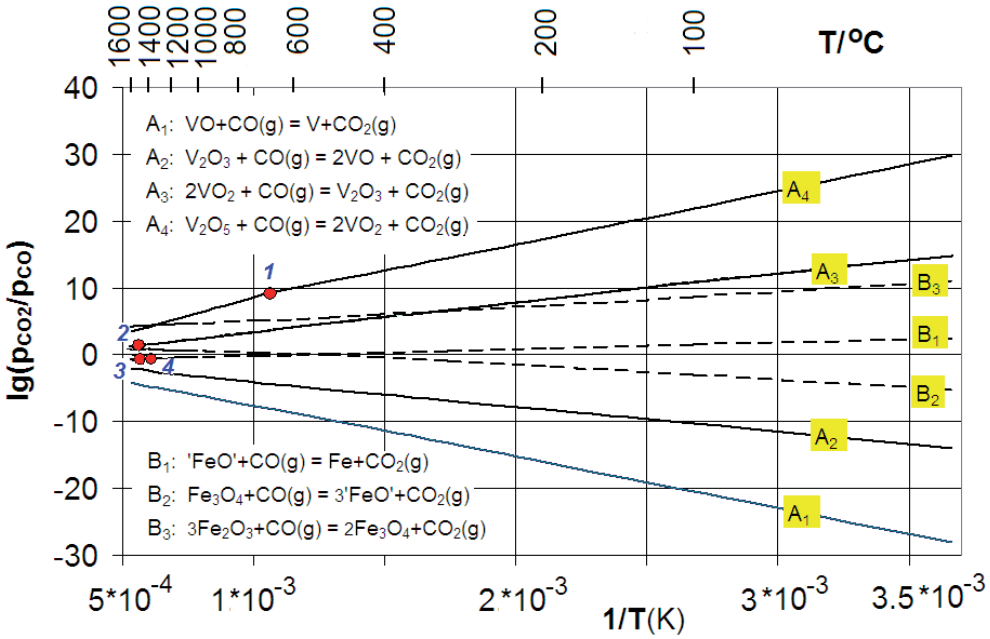

Figure 2: Equilibrium partial pressure ratio of CO_2 to CO for the oxides reduction with CO
Note: 1, 2, 3 and 4 indicate the melting points of V_2O_5, VO_2, Fe and FeO

As seen in Figure 1, in the first stage the de-hydration reaction occurs at low temperatures, $VOSO_4 \cdot 3H_2O$ decomposes into $VOSO_4 \cdot H_2O$ below 250°C, and further to $VOSO_4$ up to about 750°C. The sulphates in the ash mixture will be further decomposed into oxides and the SO_2 gas. The amount of sulphate decreases with increasing temperature at equilibrium state, and the sulphur will be eliminated from the system at about 1000°C.

Figure 2 shows the equilibrium partial pressure of CO_2 to CO for the reduction of the major constituents in the reaction system FeO_x and VO_y. The activities of the condensed reactants and products were assumed to be unity in the calculation. It shows that the reduction of iron oxides and vanadium oxides may occur simultaneously. It starts with the reduction of V_2O_5, and follows with the reduction of Fe_2O_3 in the system. Depending on the reaction driving forces, the reduction with the residue carbon in the system can be very complicated. V_2O_5 has moderate thermodynamic stability with low melting point (678°C) and somewhat volatile nature. It is easily reduced to the non-volatile oxides like VO_2, V_2O_3 and VO with higher melting points. It can be seen that reduction of vanadium oxide from V_2O_5 to metallic vanadium involves multi-stage reactions, and the final reduction stage requires a quite strong reducing atmosphere. However, at high temperatures of 1500°C and above, the formation of metallic iron and metallic vanadium requires very similar reducing conditions (P_{CO}/P_{CO2} ratio). According to the above thermodynamic calculations, the sulfur can be removed from the reaction system and the reduction with the residue carbon is theoretically possible, which gives the motivation to continue the research with high temperature experiments.

4 EXPERIMENTAL

4.1 Thermal analysis

Thermal behavior of the petroleum fly ash and BOF flue dusts were investigated with a Netzsch STA 409C thermal balance under argon atmosphere with a flow rate of 3 l/hr, for combined TGA and DTA analysis. About 20 mg of ash sample was charged in an Alsint crucible. Alumina powder was used as reference material. The furnace was gas-tight, and was heated to 1550°C with a rate of 10°C/ min, and equilibrated at 1550°C for one hour.

4.2 Carbon reduction

A vertical SiC heated tube furnace was used for the smelting tests to identify the reduction performance in the high temperature reaction system. For the reduction with the residual carbon, the ash mixture consisting of petroleum fly ash and BOF flue dust is mixed and charged in an Alsint crucible. The iron is present in the BOF flue dust in a varying ratio of metallic Fe, FeO and Fe_2O_3 depending on the process operation conditions [11]. The charging ratio of the fly ash and the BOF flue dust was calculated based on the requirement of carbon for reduction of the stoichiometric compositions of the oxides in the ash mixture including FeO_x, V_2O_5 and NiO, assuming that FeO is the major component on average, i.e. 46.3 wt% FeO in BOF-CF flue dust; 44.8 wt% VO_2, 7.5 wt% NiO and 0.98 wt% FeO in the petroleum fly ash. With a mixture of 16 g petroleum fly ash and 20 g BOF-flue dust of the coarse fraction, there is about 32.6 % extra stoichiometric carbon in the system. The actual maximum carbon consumption is estimated to be about 24.6 wt% in the fly ash (36.5 wt% total carbon). The added SiO_2 amount was estimated roughly based on the equal weight amount of available CaO and MgO in the ash mixture.

4.3 Off-gas analysis

The off-gas analyzing tests were carried out in a horizontal tube furnace in nitrogen atmosphere. A quartz tube containing an Alsint boat crucible with the ash sample was placed in the Alsint furnace tube, as schematically illustrated in Figure 3. The CO, CO_2 and SO_2 generated in the reaction system were analyzed continuously.

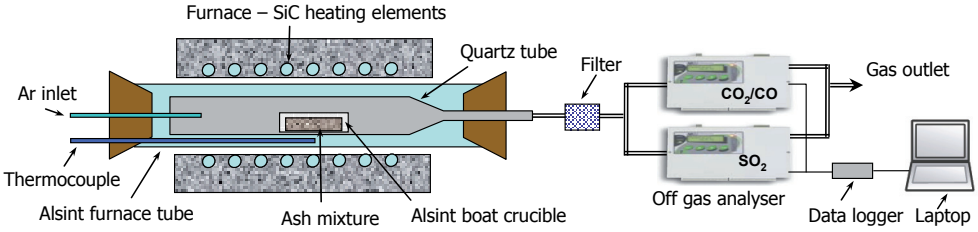

Figure 3: Horizontal “tube in tube” furnace set-up with online off-gas analysis

In addition, TGA/DSC tests for the ash mixtures were carried out to assist in understanding the reaction progress in the reaction system at elevated temperatures. After the melting experiments the slag and metal samples are analyzed with XRF. The details of the experimental conditions are given together with the results.

5 RESULTS AND DISCUSSION

To investigate the feasibility of ferrovanadium production from waste resources, the petroleum fly ash containing significant amount of vanadium oxides (and carbon) and BOF steelmaking flue dust being rich in iron oxides (and CaO) have been used as raw materials for ferrovanadium production. The residue carbon in the fly ash is used as the major reductant, while certain amount of SiO_2 was added as a fluxing agent for slag formation.

5.1 Thermal behaviour

To understand the thermal behaviour of the ash samples at elevated temperatures, thermal gravimetric analyses (TGA) were carried out separately for the three selected samples: petroleum fly ash, BOF-CF and BOG-FF, and the results are shown in Figure 4. The temperature profile was controlled at 10 °C/min linearly heating to 1550°C and then holding for about 1 hour. A significant weight loss with the petroleum ash sample is due to the de-hydration and the graduate decomposition of the sulphates, volatilization, evaporation, and even the reduction of the oxides with the existing carbon residue. Without additives, the total weight loss of the petroleum fly ash is more than 60 wt%, which is much higher than about 11% for the BOF-CF and about 6% for the BOF-FF.

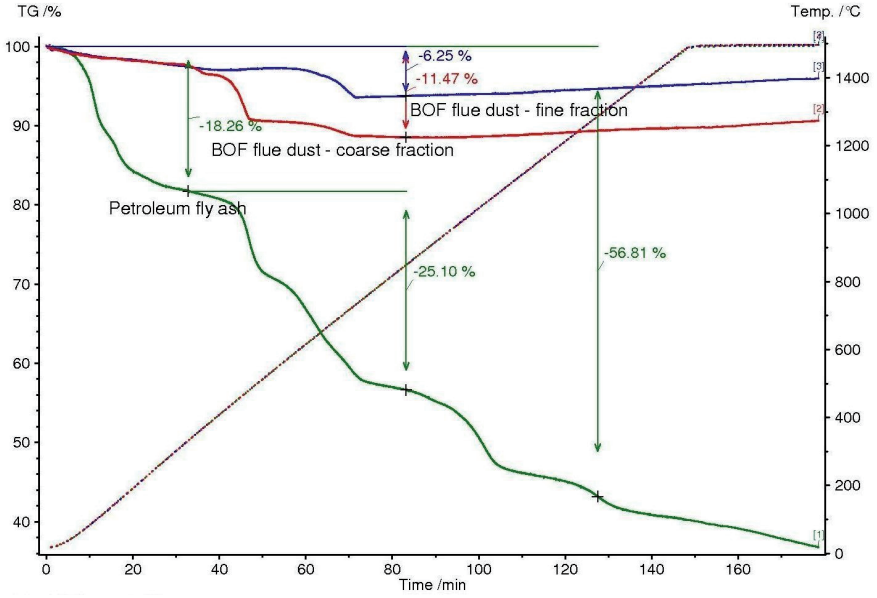

Figure 4: Comparison of the weight loss curves of the three different ash samples. Heating rate: 10°C/min under Ar atmosphere

Comparing with the thermodynamic calculation of the sulphates decomposition in Fig.1, the de-hydration and the sulphates decomposition occur in various stages at temperatures below 1200°C. DTA curves of the above reactions do not give much insight information, and is not presented here. From the TGA curves it can be observed that the reduction of oxides in the fly ash with the residue carbon proceed continuously, especially at high temperature.

5.2 Smelting tests in a vertical tube furnace

The feasibility of using the residue carbon in the petroleum fly ash to reduce the oxides in the ash mixture for FeV production has been investigated in a vertical tube furnace, and the formed slag and metal phases were analyzed for characterization. The conditions of smelting experiments are listed in Table 3. In the preliminary test B-1, B-2 and B-3, three smaller crucibles were charged with the ash

mixture as listed in Table 3, and placed into a bigger Alsint crucible for the smelting tests, and the three tests were controlled at the same conditions, smelted at 1550°C for 2 hours with a heating rate of 10°C/min, under argon atmosphere. B-4 is the scale-up of the B-1 test, and the obtained slag and metal samples are analyzed for determining the metal recovery and understanding the elemental behaviour in the reaction system.

Table 3: Ash smelting experiments in a vertical tube furnace (1550°C for 2 hours in Ar)

Test	Charge, g				BOO FA to BOF-CF ratio	Total weight, g	Weight loss, %	Metal yield, %	Remarks
	BOO FA	BOF-CF	SiO_2	C					
B-1	1.28	1.59	0.96	---	0.8	3.83	38.4	32.6	Good metal/slag separation
B-2	1.07	1.33	0.81	0.07	0.8	3.28	42.4	---	No metal agglomeration
B-3	0.95	1.59	0.95	---	0.6	3.49	31.8	31.4	Metal yield in total ash
B-4	16.0	20.0	12.0	---	0.8	48.0	36.4	27.3	mixture

Table 4: Major compositions of slag and metal

Test	Slag, wt%						Metal, wt%		
	CaO	SiO_2	MgO	FeO	VO	NiO	Fe	V	Ni
B-1	28.3	35.6	6.50	15.6	0.13	0.07	63.0	18.2	1.89
B-3	26.0	44.8	5.25	12.4	0.19	0.05	62.2	20.8	1.15
B-4	33.6	38.6	7.23	4.58	0.96	0.10	62.4	22.6	1.88

In general, the metal yield from the ash mixture is about 30wt%, and in the obtained alloy the vanadium contents are in the range of 18 – 23 wt% under the present experimental conditions. The nickel contents are between 1 to 2 wt%, as seen in Table 4. There are significant amounts of impurities entrapped in the alloy, possibly some carbide and slag in the metal phase, to be further investigated.

According to the results of XRF analyses on the slag and the produced metal, the heavy metals of Zn and Pb go mainly into the secondary flue dust with the off-gas, while Cu is distributed in all phases. The total amount of the heavy metals is relatively low in the present system. To obtain a more reliable element distribution and mass balance among metal, slag and off-gas, larger scale smelting tests are to be conducted.

5.3 Smelting tests in a horizontal tube furnace with on-line off gas analysis

To further understand the reduction behaviour, the reaction off gas was analyzed continuously on-line in a horizontal tube furnace. The two tests are given in details in Table 5, and the recorded off-gas analysis is shown in Figures 5 and 6. C-1 test was designed to use both Al and residue carbon as the reductants in the reaction system, and many fine metal beads were formed, no agglomerated metal phase was formed due to the presence of significant amounts of extra carbon. B-5 has the same composition as in the test B-1 and B-4.

Table 5: Tests with off gas analysis

Test	Charge, g					Total weight, g	Weight loss, %	C, g in off gas	Total, CO, g	Total CO2, g	C/BOO-FA, wt%	Remarks
	BOO FA	V-Af. LOI	BOF-CF	SiO_2	Al							
C-1		2.42	3.81	2.29	1.81	10.3	23.2	0.493	0.213	1.278	20.3	No homogeneous melt formation
B-5	2.83		3.54	2.12		8.50	39.4	0.579	0.932	0.666	20.5	With distributed metal beads

Note: C-1 test was conducted at 10°C/min, N_2, 1550°C. (V-Af. LOI) is the petroleum fly ash after low temperature loss on ignition test. (C/BOO FA) represents the percentage of carbon going into off gas in the fly ash.

It can be seen that for the cases of B-1, B-3, B-4 and B-5 tests, in general the weight loss is in the range from 36.4 to 42.4 wt%, with the metal yield of 20.5 to 24.4 wt%. The weight loss is contributed by volatile matter in the ash, the dehydration, decomposition of sulphate components, the reduction reaction of the oxides with the residue carbon, and the secondary flue dusts containing the metal vapour such as heavy metals etc. which were carried away with the off gas. The weight loss with Al

reduction (C-1) is 23.2%, which is about 16% lower than that with the residue carbon in the fly ash. Regarding the sulphate decomposition, SO_2 is constantly generated starting at low temperature which needs to be further investigated.

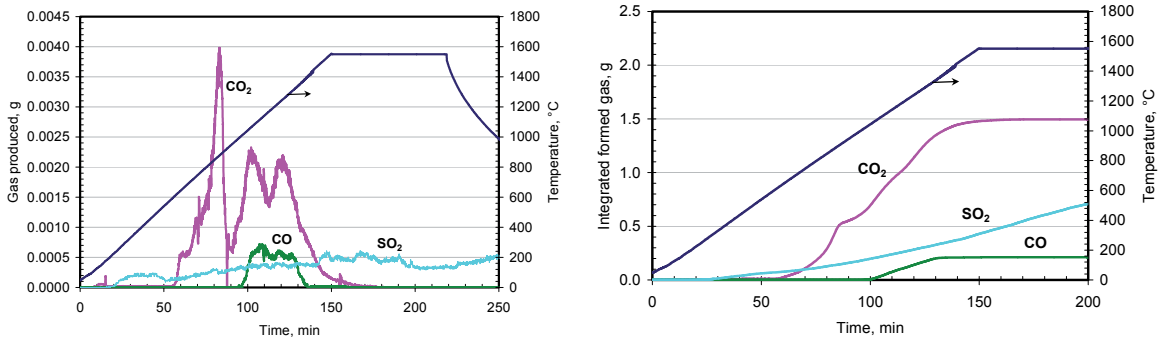

Figure 5: Off-gas analysis of the C-1 test: petroleum fly ash (after LOI test) and BOF flue dust mixture with SiO_2 and Al addition – reduction with the residual carbon and the added Al in the ash; 10°C/min under N_2 atmosphere, equilibrated at 1550 °C.

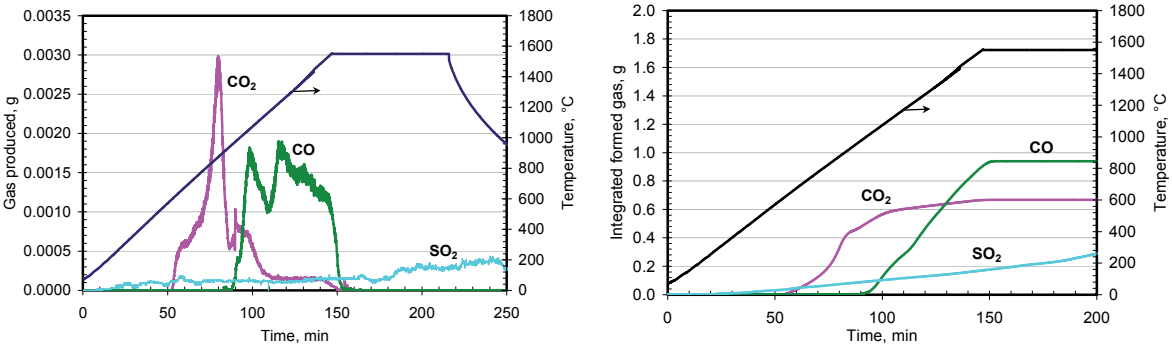

Figure 6: Off-gas analysis of B-5 test: petroleum fly ash and BOF flue dust coarse fraction mixture with additive of SiO_2– reduction with the residual carbon in the ash; 10 °C/min under N_2 atmosphere, equilibrated at 1550 °C.

Figure 7 shows the thermal analysis (TGA/DSC) of the three ash mixtures as is shown in Table 6. A continuous weight loss (higher than 50 % in total) is observed for the mixture of petroleum fly ash and BOF-CF without silica addition. The weight loss was reduced to about 35% with the addition of SiO_2 for slag formation. With the addition of aluminium in the system, there is even less weight loss with the Al_2O_3 formation. At the low temperatures between approximately 25 and 800ºC, the weight loss was mostly caused by the volatilization, dehydration and decomposition of sulphates in the sample. At about 400ºC a weight loss occurred for all three samples, due to the dehydration of the $VOSO_4.xH_2O$.

Table 6: TGA-DSC tests of the ash mixtures

TGA-DSC Test	Ash mixture
D-1	Petroleum fly ash and BOF –CF flue dust with 4:5 in weight ratio
D-2	Petroleum fly ash and BOF –CF flue dust with 4:5 in weight ratio + SiO_2
D-3	Petroleum fly ash and BOF –CF flue dust with 4:5 in weight ratio + SiO_2 + Al

For the sample with Al addition (test D-3), the melting peak of metallic aluminium is shown in the DSC curve, corresponding with no extra weight loss. From the DSC-signal it can be inferred that slag formation takes place at about 1350ºC for the samples with silica addition. These phenomena were further illustrated in the DDSC curves, as shown in Figure 7. The dramatic change in the DSC-curve starting at approximately 1350ºC, not only indicates a reduction reaction, responsible for the simultaneous weight loss, but probably also indicates the onset of melting of the sample mixtures.

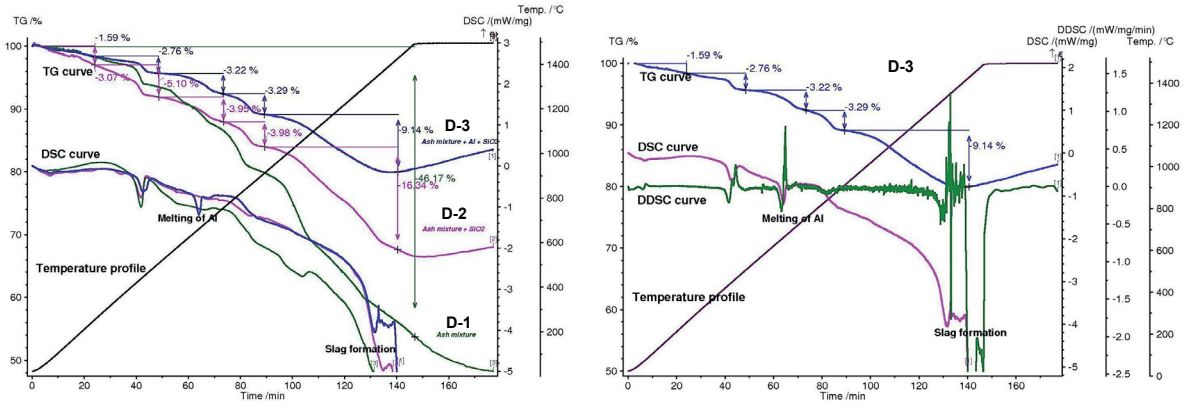

Figure 7: Thermal analysis of the ash mixture of the petroleum fly ash and the BOF flue dust (Coarse fraction) with or without additives (Al as additional reductant and SiO_2 as fluxing agent for slag formation). Heating rate: 10°C/min under Ar atmosphere

5.4 Perspectives

It is demonstrated through laboratory scale experiments that ferrovanadium with about 20 wt% V content is obtained with the stoichiometric mixture without additional carbon addition, which has the advantages of using the waste based materials with high environmental benefit and resource saving. The high impurity level in the alloy phase was caused partly by the non-metallic inclusions, according to microscopic analysis (to be confirmed by SEM, EPMA). The impurities in the formed alloy phase will need a further refining step, to be investigated in the following research. For the feasibility of adopting the waste streams for the ferrovanadium production, the sulphur issues and the economic factors need to be further investigated. Low melting point of V_2O_5 may have some kinetic influence on the slow decomposition of $VOSO_4$. The vanadium slag properties will be affected by the oxygen potentials in the system, and the formation of lower VO_x will have significant influence on the reducibility of the oxides and melting temperature of the slag.

In the present research, the ash mixture was heated very slowly in the laboratory-scale furnaces, and vanadium recovery in metallic form has reached about 50%. Still significant amount of vanadium is reported to the slag phase or to the secondary flue dust due to high vapour pressure of the high valence vanadium oxides such as V_2O_5. The high carbon content in the alloy can be adjusted by designing the whole process into stages, the pre-reduction with the residual carbon, and followed with the final reduction with additives of FeSi or Al to achieve higher metal recovery from the system.

The advantages of the direct high temperature processing of the petroleum fly ash are the direct use of the residue carbon in the raw material, and the potential of optimum combination of the secondary (waste) materials for producing a value added intermediate or final product. However, the great challenges are due to the complicated ash compositions, especially the existing form of sulphur which may complicate the process if without pre-treatment for sulphur removal. The present research reveals that sulphate decomposition in the ash mixture is a relatively slow process, according to the recorded SO_2 analysis. The effects of mixing and briquetting and additions of different reducing agents and slagging/fluxing components on the smelting results will be systematically studied. The behaviour and distribution of heavy metals will also be investigated in the next stage research. The slag formation and reduction with residue carbon, in comparison with metallothermic reduction using Al and/or FeSi will be further studied. The possibility of selective control of the elements flow will be explored, leading to the concentrated secondary flue dust with high heavy metal contents for the zinc/lead industry.

Utilizing the secondary vanadium resource is important not only for saving the raw materials resource, but also for closing the vanadium cycle, thus reducing the environmental impact. The major factors to be considered in the future will be the design of a low cost process with a high-valuable product and a well designed closed loop processing with no or less harmful environmental foot prints.

6 CONCLUDING REMARKS

The present study demonstrates the feasibility of combined processing of petroleum fly ash and BOF steelmaking flue dust for ferrovanadium production. According to the thermodynamic evaluation and laboratory-scale experimental results, the following conclusions can be obtained:

a) The high carbon content in the petroleum fly ash can be used as reductant for reduction of iron oxide in BOF flue dust and the vanadium oxides in the petroleum fly ash. A ferrovanadium alloy with about 20wt% V is obtained at 1550ºC, with certain addition of silica for slag formation. On average about 30% of metal yield was obtained during smelting of the ash mixture with the petroleum fly ash to BOF flue dust (coarse fraction) in 4:5 in weight ratio.

b) The thermodynamic prediction indicates that sulfur in the fly ash can be removed from the system at temperatures below 1200 ºC, however, there is still a lot of entrapped sulfur in the slag and metal phases. Kinetic factors in sulfates decomposition may play important roles, which deserves further detailed study.

c) To meet the stricter environmental regulations for the solid waste disposal in the future, a recipe based combined waste processing can be a sustainable and economical option, if a market valuable metal product can be produced. The benefits are both resource saving and providing a better environmental solution.

7 ACKNOWLEDGEMENTS

The authors would like to acknowledge CORUS for providing the BOF flue dust samples and Greenshores N.V. for providing the petroleum fly ash for the experiments; Z. Zhang for conducting the thermal analysis of the ash samples; J. van den Berg and R. Hendrikx at the Department of Materials Science and Engineering of Delft University of Technology are acknowledged for the LECO and X-ray analysis.

8 REFERENCES

[1] U.S. Geological Survey, 2009, Mineral Commodity Summaries 2009: U.S. Geological Survey, p.181.
[2] Ye, G., “Recovery of Vanadium from LD slag, a state of the art report, Part 1- Facts and metallurgy of vanadium”. Report JK 88031, 2006-04-05, ISSN 0280-249X.
[3] Moskalyk, R.R. and Alfantazi, A.M., “Processing of vanadium: a review”, Minerals Engineering 16 (2003) 793-805.
[4] Gupta, C.K. and Krishnamurthy, N., “Extractive Metallurgy of Vanadium”, Elsevier, Amsterdam, 1992, p.441.
[5] Gupta, C.K., “The aluminothermic process for vanadium production”, Proceedings of the International Symposium on Vanadium, Conference of Metallurgists, Montréal, Canada, CIM, Aug. 11 – 14, 2002, pp.205-225.
[6] Mambote, C.R., Xiao, Y. and Schuiling, R. D., “Vanadium Recovery from Fly Ash – a Review”, Proceedings of XXIV International Minerals Engineering Congress – IMPC 2008, Eds. D.Z. Wang, C.Y. Sun, F.L. Wang, L.C. Zhang and L. Han, Beijing, China. Science Press, Beijing, 24-28 Sept. 2008, pp.3697-3707, ISBN number: 978-7-03-022711-9.
[7] Pickels, C.A. and Alcock, C.B., “Production of ferronickel and ferrovanadium from fly ash in an extended arc reactor”, Journal of Metals 35 (1983), pp.40 – 45.
[8] Abdel-latif, M.A., “Recovery of Vanadium and Nickel from Petroleum Flyash”. Minerals Engineering 15 (2002) 953-961.
[9] http://www.metalpass.com/metaldoc/paper.aspx?docID=608
[10] Roine, A., HSC Chemistry 6. Outotec Research Oy, Pori, Finland.
[11] Nedar, L., “Dust formation in a BOF converter”, Steel Research 67 (1996) No.8, pp.320 – 327.