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High Temperature Processing of Secondary Metallurgical Resources

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Abstract

Bottom ash, slag, fly ash and flue dusts are solid wastes or by-products from thermal waste processing or pyrometallurgical process operations. They bear potential environmental risks due to the presence or accumulation of certain heavy metals and hazardous elements. On the other hand they have potential economic value, being secondary resources containing various valuable metals. Research activities of high temperature processing of various secondary resources at Delft University of Technology are introduced. Three cases are discussed in detail: the vitrification of solid waste and incineration residues and the thermodynamics of the vitrified slag; zinc recovery from zinc ferrite-bearing industrial residues; and the vanadium recovery from the fly ash in heavy oil fuelled power plants. A recipe-based combined waste processing concept is introduced for the industrial waste management. An example is given for ferrovandium production from Basic Oxygen Furnace (BOF) flue dust and the fly ash from heavy oil fuelled power plant. In addition, the future perspectives of the high temperature processing of secondary resources are addressed.

Introduction

Environmental protection and proper waste management are essential for our human society. With commercial interests, continuous exploitation of the natural resources seems to be inevitable. More process wastes may be expected due to the lower grade of raw material feed for the primary metallurgical industry. On the other hand, increasing recycling activities by introducing more complex secondary resources in primary sector may also create by-products or secondary wastes. A good waste management system should consider various factors including the waste minimisation, resource recovery, recycling and reuse to limit the level of disposal. The waste generated in metal industry usually still contains certain valuable elements, and it is regarded as the secondary resource. By the growing recognition of depleting natural resources, new technologies need to be developed to serve the effective waste management. High temperature processing is one of the options for the waste treatment. However, the inherent features in the processing need to be better understood, such as energy consumption, the secondary environmental

pollution and waste generation, product quality control, and the marketability. In the present paper, a few research cases are given for a better understanding of the metal recovery from the secondary resources, including municipal solid wastes incineration (MSWI) bottom ash, zinc bearing residues, fly ash from heavy oil fuelled power plant, and the basic oxygen furnace (BOF) flue dust. The related fundamental issues in understanding the reaction mechanism for a better process control are investigated.

Table 1 lists the chemical compositions of the processed solid waste materials. The carbon content in the test samples was determined with a LECO CS225 induction furnace, and semi-quantitative X-ray fluorescence spectroscopy (XRF Phillips model PW2400) was used to determine the (elemental) chemical composition. The mineralogical phases were identified with X-ray diffraction (XRD Siemens model D5005), and observed with scanning electron microscope (SEM JEOL JSM 6500F) and analysed with electron microprobe analysis (EMPA) or energy-dispersive X-ray spectroscopy (EDS). To understand the thermal behaviour of the samples, the TGA/DSC tests (NETZSCH STA 409 C/CD) were conducted, and the reaction kinetics were also monitored with an on-line gas analyser, when it is necessary, including the gas evolution rate of CO, CO₂ and SO₂.

Table 1: Compositions of the representative samples (XRF and LECO analysis, wt%) (Bottom ash, Rotterdam Harbour residues- RH Zinc B, V-fly ash and BOF dust)

Element	Fe	V	Ni	Si	Ca	Al	Mg	S	P	Na	K
Bottom ash	7.61	0.03	0.10	26.70	9.00	3.86	1.02	0.67	0.35	4.01	0.91
RH Zinc B	35.67	0.01	0.03	1.38	5.07	0.54	1.68	0.35	0.08	0.82	0.71
V-Fly ash	0.77	27.56	5.93	0.27	0.79	0.06	2.65	12.75	0.02	1.39	0.08
BOF-dust	36.03	0.03	0.01	0.71	42.55	0.22	7.40	0.05	0.01	0.05	0.05
Comp. wt%	Ti	Cr	Mn	Zn	Pb	Cu	Cd	Cl	C (LECO)	SUM	S (LECO)
Bottom ash	0.55	0.10	0.09	0.29	0.15	0.32	0.01	2.20	n.a.	57.96	n.a.
RH Zinc B	0.05	0.33	5.00	17.50	1.85	0.12	0.02	0.83	n.a.	72.03	n.a.
V-Fly ash	0.13	0.00	0.02	0.05	0.06	0.05	0.00	0.00	36.50	89.10	12.30
BOF-dust	0.07	0.02	0.63	0.19	0.01	0.01	0.00	0.03	0.57	88.60	0.00

Metal recovery from MSWI bottom ashes and thermodynamics of the vitrified slag

During incineration of municipal solid waste, various environmentally harmful elements and heavy metals are liberated either into bottom ash, or carried away with the off-gases and subsequently trapped in fly-ash. If these minor but harmful elements are not properly isolated and immobilised, it can lead to secondary environmental pollution to the air, soil and ground water. The stricter environmental

regulations require a higher immobilisation efficiency of the bottom ash treatment. Physical separation technologies play significant roles in metals recovery, but it also shows a limited efficiency especially for metal recovery from the fine fractions. The bottom ash from AVR, a Dutch MSWI, was vitrified at higher temperatures and the formed slag and the recovered metal were examined.¹ To provide fundamental knowledge on the chemistry of the related slag, the phase relations of Na₂O-containing slags have been investigated.²

Vitrification of the bottom ash

In the Netherlands, bottom ash originated from the MSWI contains typically about 18% metals, and the current industrial practice could recover about 10% metals through magnetic and eddy current separators. The remaining 8% in the finer fractions is difficult to recover through current physical separation technology. Among various alternatives, vitrification is one of the promising options to immobilise the ash and recover the remaining metals.

Vitrification is an ash melting and solidification process at 1400 – 1500°C, leading to high destruction efficiency of organics, immobilisation of environmental harmful elements in the ash, and volume reduction. During vitrification a homogeneous glassy slag and a Fe-Cu based alloy are obtained. In this study,¹ the recovered metal alloy contains about 82 wt% Fe, 12 wt% Cu and 6 wt% other alloying elements and impurities such as C, S, P, Ni *etc.* The metal composition is very close to that of the metal product from other MSW thermal processing processes such as Thermoselect.³ However, the generated alloy does not have direct commercial applications as steel scrap or copper scrap. Copper is either too high for steelmaking plant, or too low for copper smelter, and separation and recovery of copper from iron-based alloy are critical to obtain the market value of both copper and ferrous constituents. Figure 1 illustrates a typical bottom ash generated from a WtE (Waste-to-Energy) plant and the vitrified slag and metal alloy products from laboratory vitrification tests. Copper removal from the alloy has been investigated by using waste sulphide minerals or sludge, and interesting results were obtained.⁴

In general, it is known that MSWs contain metals of Fe, Al, Cu, Zn and Pb *etc.* in decreasing order. As the biggest urban mine, the metals extraction is far from efficient and ideal, and metals, especially the non-ferrous metals are lost during the various steps of the waste treatment. For example, with less efficient pre-separation, the aluminium and other active metals in small size will be burned during the incineration. Regarding the resource recovery, the future waste management can be improved by combining the available advanced sorting techniques and modifying the incineration conditions. Pre-sorting of MSW before incineration is practised in certain countries, but a careful cost-benefit analysis must be made.

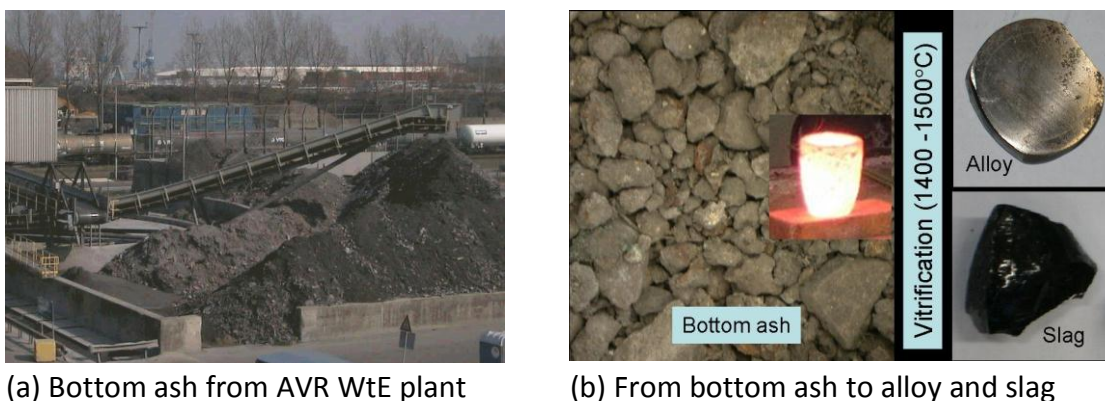


Figure 1: Bottom ash and the vitrified products

Slag thermodynamics

The complex bottom ash formed during MSW incineration can be transformed into glassy slag by vitrification as shown in Figure 1. In the bottom ash, SiO_2 , CaO , Al_2O_3 , Fe_2O_3 , Na_2O and MgO account for more than 90% by weight, which have direct effect on the glass formation during vitrification. The ternary system Na_2O - CaO - SiO_2 was found to be important for the phase relations during the thermal processing of the bottom ash, especially in the low silica region (less than 50 wt% SiO_2), where different crystalline phases will be present during high temperature treatment, depending on the composition of the bottom ash. This ternary system has been investigated in the literature in the composition region with relatively lower Na_2O contents and higher SiO_2 contents.⁵⁻⁹ The thermodynamic study of the slag systems with high Na_2O is a challenging task due to the vaporising of Na_2O at high temperature.

In the research group MPRR, equilibrium phase relations in the Na_2O - CaO - SiO_2 system at less than 50 wt% SiO_2 have been experimentally investigated at temperatures between 1200C to 1400C under air atmosphere.² The liquidus temperature was determined with differential scanning calorimetry (DSC). The equilibrated samples were quenched with high pressure nitrogen, and examined with EPMA and XRD. Based on the experimental results and the compositions of the equilibrated samples, the liquidus surface projection has been constructed for this temperature range. Six primary phase fields, Ca_2SiO_4 , $\text{Ca}_3\text{Si}_2\text{O}_7$, CaSiO_3 , $\text{Na}_2\text{Ca}_2\text{Si}_3\text{O}_9$, $\text{Na}_2\text{Ca}_2\text{Si}_2\text{O}_7$ and $\text{Na}_2\text{CaSiO}_4$ were identified, as shown in Figure 2. The phase diagram has also been calculated based on the obtained experimental results and the slag models, which provide fundamental knowledge on the industrial application of the vitrified bottom ash slag.

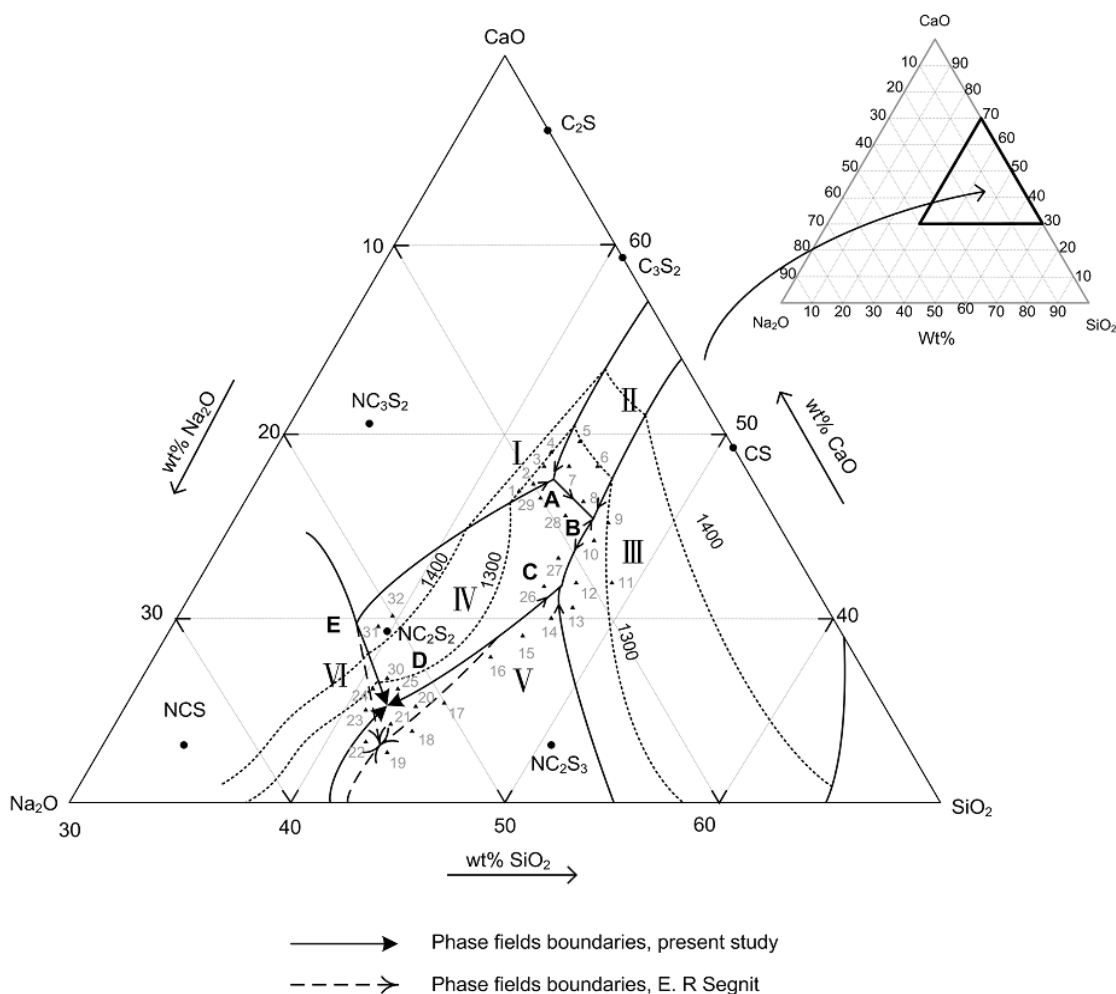


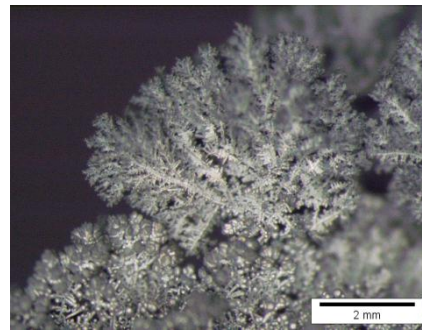
Figure 2: Primary phase fields and liquidus surface projection of the system Na₂O-CaO-SiO₂ containing Na₂O (0 - 40 wt%) and SiO₂ (30 - 70 wt%). The primary phase fields of Ca₂SiO₄, Ca₃Si₂O₇, CaSiO₃, Na₂Ca₂Si₂O₇, Na₂Ca₂Si₃O₉, and Na₂CaSiO₄ are represented by I, II, III, IV, V and VI, respectively. (C = CaO; N = Na₂O; S = SiO₂).

Zinc recovery from industrial residues

In Rotterdam harbour there is about 4700 tons of zinc containing materials, stored there for 18 years without proper treatment solutions. These zinc-bearing materials have a relatively low zinc content, and cannot be used in any zinc smelters (both hydrometallurgical and pyrometallurgical) as raw materials, without zinc enrichment processing. Because of the presence of some other elements such as chlorine, lead and a small amount of other heavy metals, they cannot be landfilled. A feasibility study for metallurgical processing of zinc bearing materials was conducted in MPRR group. Based on the chemical and structural analyses of the solid materials, as well as the preliminary experimental results from the laboratory tests, various alternative conceptual treatment flowsheets are proposed for in-depth experimental research and development in the laboratory. The synthesised technological routes are further



Zinc B



Electro-wonned Zn

Figure 3: RH Zinc B and produced zinc metal via leaching and electrowinning

studied through laboratory experiments in order to develop proper operating conditions and parameters which are needed for designing larger scale treatment facilities, such as a pilot scale treatment plant. Figure 3 shows the raw material (RH Zinc B), and the recovered metallic zinc through alkaline leaching (5 M NaOH at 90°C for 1 hour) and electro-winning in the lab. Following the leaching route, a total recovery of 74% has been obtained. At the same time, 71% of lead has also been recovered. Cementation of impurities and electro-winning of zinc were technically feasible; however optimisation is needed to obtain products with expected purity. The final residue could be potentially used as a raw material for ironmaking after proper treatment to remove residual zinc and sodium.

The zinc in the form of ZnO can be easily leached and recovered. However, zinc in the form of ZnFe_2O_4 is difficult to be dissolved, requiring pyrometallurgical processing or leaching under special conditions, *e.g.* in an autoclave.^{10,11} As a reference case, high temperature pyrometallurgical carbothermic reduction of the materials has also been studied at MPRR group.

The pyrometallurgical approach has the advantage to reduce the zinc ferrite into metallic zinc with carbon. This type of operation has been in industrial practice for treatment of EAF steelmaking flue dust or neutral leach residues of hydrometallurgical zinc production plant such as the Waelz Kiln process for upgrading the zinc content.¹² The current study aims to verify whether this type of zinc-bearing residue will work effectively with the pyrometallurgical fuming process, and to understand how zinc and iron oxides/compounds behave under carbothermic reduction conditions.

Thermodynamic analysis

The high temperature thermodynamic stability of the major components in the concentrate (*i.e.* zinc ferrite, $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$) is evaluated with HSC chemistry, and the results are given in Figure 4. It can be predicted that in the first stage the Fe_2O_3 in the

ferrite is reduced with carbon, forming Fe_3O_4 and ZnO starting at low temperatures ($\sim 400^\circ\text{C}$), where CO_2 is the major gas product. At around 700°C , reduction of Fe_3O_4 to FeO ($\text{Fe}_{0.94}\text{O}$) has reached a maximum. From this point, metallic iron starts to form and is completed at 750°C . The oxides reduction continues with increasing temperature, and zinc will be produced at a temperature of about 800°C and at the temperature above 900°C (zinc boiling point: 907°C) mainly zinc vapour is formed as the main product. Production of zinc is generally completed at about 1200°C . According to this calculation, thermal decomposition of zinc ferrite at relatively low temperatures through partial carbothermic reduction of Fe_2O_3 could convert the ferrite to free ZnO and FeO/Fe . This will have potential of using hydrometallurgical leaching of the residue to recover zinc.

Reduction experiments

The feed mixture was prepared with 50 grams of the concentrate RH Zinc B, which was mixed with 6 grams of graphite powder and 6.2 grams of SiO_2 as fluxing agent for proper slag formation. For a comparison, pure ZnFe_2O_4 of 4.25 g was mixed with 0.85 g carbon, *i.e.* 20 wt% (theoretical stoichiometric ratio is 16.6 wt% carbon). An Alsint boat crucible holding the feed was placed in a horizontal tube furnace. The CO and CO_2 generated in the reaction system were analysed continuously with an online gas analyser under Ar atmosphere. The sample was heated at a rate of $10^\circ\text{C}/\text{min}$, and kept at 1500°C for one hour. The charging ratio of the zinc concentrate, carbon and fluxing agent was calculated based on the requirement of carbon for reduction of the stoichiometric compositions of the oxides in the concentrates including FeO_x and ZnO , assuming that iron is present mainly as Fe_2O_3 originally bound with ZnO . The added SiO_2 amount was estimated roughly based on the equal weight amount of available CaO and MgO in the sample. Figure 5 shows the reduction kinetics of the

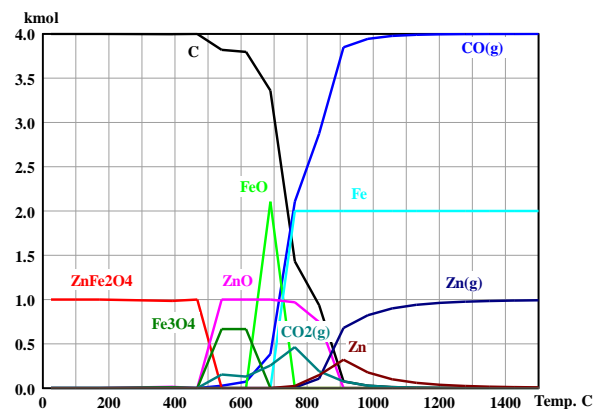


Figure 4: Thermodynamic prediction of ZnFe_2O_4 reduction with the stoichiometric amount of carbon

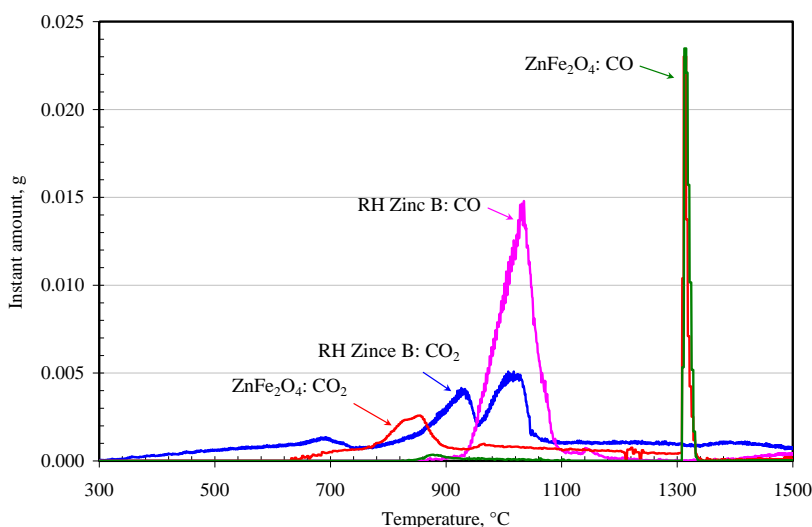


Figure 5: Off-gas analysis of Rotterdam Harbour's residues (RH Zinc B) with additive of carbon and SiO_2 ; in comparison with the reduction of pure zinc ferrite with carbon $10^\circ\text{C}/\text{min}$ under N_2 atmosphere, equilibrated at 1500°C

feed (RH Zinc B) measured with the on-line gas analyser, in comparison with the reduction of pure ZnFe_2O_4 under the same conditions.

The CO/CO_2 gas evolution along heating process provides a lot of information about the oxide reduction process. For the RH Zinc B, CO_2 starts to form at about 400°C due to the reduction of Fe_2O_3 , which corresponds to the first peak of CO_2 formation at the temperature lower than 700°C . Reduction of lead and copper oxides takes place most likely at about 800°C (corresponding to the second CO_2 peak), and reduction of zinc oxide occurs at around 900°C and reaches the maximum at approximately 1000°C . It is clear that most of the carbothermic reductions are completed at around 1100°C . The CO_2 generated at higher temperatures is most likely due to the reduction of remaining ZnO and FeO , as well as decomposition of CaCO_3 . After reduction, metallic iron was formed in the melt which contains 92% Fe and 2.5% Mn and minor Si and Cu. The reduced zinc is vaporised and collected as a powder mixture of zinc metal and zinc oxide in the gas filter system. However, for the reduction of pure zinc ferrite, the recorded CO and CO_2 generation rate is quite different comparing to that predicted from thermodynamic calculations. The formation of both CO and CO_2 are delayed, and higher temperature (e.g. 1350°C) is practically required for the reduction of ZnFe_2O_4 .

Similar to the Waelz kiln process, carbothermic reduction is technically feasible for processing the zinc residues, but it is not easy to obtain the metallic zinc product. The final zinc product would still be the upgraded zinc oxide, which could be sold to zinc

smelters for final metal production. If the objective of processing the zinc bearing residues is to produce metallic zinc, the hydrometallurgical route is more favourable and it requires a pyrometallurgical decomposition process for zinc ferrite; however, if the aim is to process it into a saleable higher grade secondary raw material for zinc smelters, the pyrometallurgical carbothermic reduction process is more appropriate. Which process to use depends on the total processing cost and the market price of zinc.

Recipe-based combined waste processing

A power plant fuelled with petroleum heavy oils generates solid residues that 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, ranking the No. 3 after the primary resource of the ore concentrates and the V-bearing metallurgical slag. According to the information in the literature,¹³ hydrometallurgical processing is usually regarded as the preferred route for the recovery of vanadium from the fly ash, due to the relatively low operating and energy cost. 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 ferrovandium through selective reduction.¹⁴ Abdel-latif¹⁵ reported an alternative flowsheet to recover vanadium from the fly ash for ferrovandium production: drying, decarburisation, desulphurisation and smelting reduction with aluminium or ferrosilicon. In both of these studies, 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. Steelmaking flue dust contains quite a high amount of iron oxides (up to 85% after drying), and a relatively low heavy metal content, depending on the quality of the scrap charge. Typically, it is recycled within the steel plant in the sintering process as the charging material into the ironmaking 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 Zn and Pb will be accumulated in the flue dust. When the concentration of the heavy metals is sufficiently 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 zinc content in the flue dust.

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 utilise 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. In the present study, a

prospective investigation is conducted to recover the metal values for FeV production from two industrial waste resources - the petroleum fly ash and BOF flue dust by using the carbon in the fly ash as reducing agent. The process feasibility is evaluated based on thermodynamic calculations. As a major vanadium source in the petroleum fly ash, the thermal behaviour of $\text{VOSO}_4 \cdot x\text{H}_2\text{O}$ is experimentally investigated. The high temperature behaviour of the fly ash and flue dust is examined with a combined approach of chemical, thermal and off-gas analyses. Metal recovery, the behaviour and control of sulphur and carbon in the system are discussed.

The main reactions in the mixture of the V-bearing fly ash and BOF flue dust are the decomposition of vanadium sulphate hydrates and NiSO_4 , followed by the carbothermic reduction of metal oxides in both the fly ash (vanadium and nickel oxides) and BOF flue dust (iron oxides), as shown below:

- a) Dehydration and sulphates decomposition of the fly ash: $< 1000^\circ\text{C}$

$$\text{VOSO}_4 \cdot 3\text{H}_2\text{O} (\text{s}) = \text{VO}_2 (\text{s}) + \text{SO}_2 (\text{g}) + 0.5 \text{O}_2 (\text{g}) + 3 \text{H}_2\text{O} (\text{g}) \quad (1)$$

$$\text{NiSO}_4 (\text{s}) = \text{NiO} (\text{s}) + \text{SO}_2 (\text{g}) + 0.5 \text{O}_2 (\text{g}) \quad (2)$$

$$\text{SO}_3 (\text{g}) = \text{SO}_2 (\text{g}) + 0.5 \text{O}_2 (\text{g}) \quad (3)$$
- b) Solid-gas reduction of oxides: $1000 - 1400^\circ\text{C}$

$$\text{FeO} (\text{s}) + \text{CO} (\text{g}) = \text{Fe} (\text{s}) + \text{CO}_2 (\text{g}) \quad (4)$$

$$\text{VO}_2 (\text{s}) + 2\text{CO} (\text{g}) = \text{V} (\text{s}) + 2\text{CO}_2 (\text{g}) \quad (4\text{a})$$

$$\text{NiO} (\text{s}) + \text{CO} (\text{g}) = \text{Ni} (\text{s}) + \text{CO}_2 (\text{g}) \quad (4\text{b})$$

$$\text{CO}_2 (\text{g}) + \text{C} (\text{s}) (\text{residue in fly ash}) = 2\text{CO} (\text{g}) \quad (5)$$
- c) Smelting reduction: $> 1400^\circ\text{C}$ (assuming ash melting and slag formation at 1400°C)
$$(\text{FeO}) (\text{l}) + \text{CO} (\text{g}) = \text{Fe} (\text{l}) + \text{CO}_2 (\text{g}) \quad (6)$$

$$(\text{VO}_2) (\text{l}) + 2\text{CO} (\text{g}) = [\text{V}]_{\text{Fe}} (\text{l}) + 2\text{CO}_2 (\text{g}) \quad (6\text{a})$$

$$(\text{NiO}) (\text{l}) + \text{CO} (\text{g}) = [\text{Ni}]_{\text{Fe}} (\text{l}) + \text{CO}_2 (\text{g}) \quad (6\text{b})$$

$$\text{CO}_2 (\text{g}) + [\text{C}]_{\text{Fe}} (\text{l}) = 2\text{CO} (\text{g}) \quad (7)$$

Figure 6 shows the calculated equilibrium partial pressure of CO_2 to CO for the reduction of the major constituents in the reaction system, being FeO_x and VO_y . It shows that the reduction of iron oxides and vanadium oxides may occur simultaneously. It starts with the reduction of V_2O_5 , followed 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 a moderate thermodynamic stability with a low melting point (678°C) and somewhat volatile

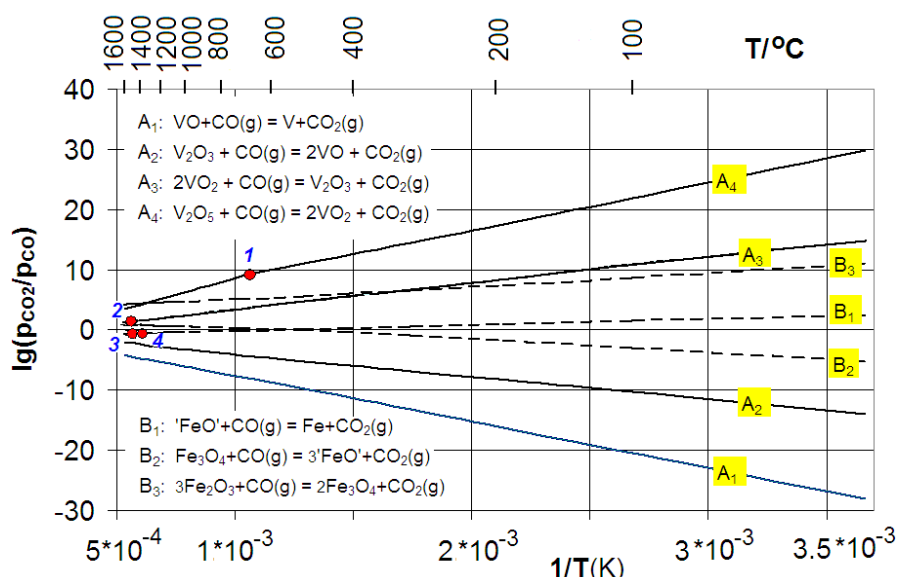


Figure 6: Equilibrium partial pressure ratio of CO_2 to CO for the oxides reduction with CO (Note: 1, 2, 3 and 4 indicate the melting points of V_2O_5 , VO_2 , Fe and FeO).¹⁶

nature. It is easily reduced to the non-volatile oxides such as 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 ($p_{\text{CO}}/p_{\text{CO}_2}$ ratio). According to the above thermodynamic calculations, the reduction with the residue carbon is theoretically feasible.

Figure 7 shows the experimentally measured profiles of gas evolution as function of temperature under Ar atmosphere. Please keep in mind that the reduction of the oxides is through carbon in the fly ash (either elemental carbon or hydrocarbons). It can be seen that decomposition of metal sulphates (vanadium and nickel) starts at about 200°C , but very slowly proceeds at elevated temperatures. Even at a temperature of 1550°C , the decomposition still goes on, as indicated by the evolution of SO_2 gas. Slag analysis indicated that still a significant amount of sulphur remains dissolved in the slag. Both CO_2 and CO gas generation show two peaks, and these may correspond to the reduction of iron oxides and vanadium oxides. It is evident that Boudouard reaction ((5) or (7) above) is predominant at temperatures above 1000°C . At about 1550°C , generation of CO and CO_2 has almost stopped, which indicates the completion of the reduction reactions.

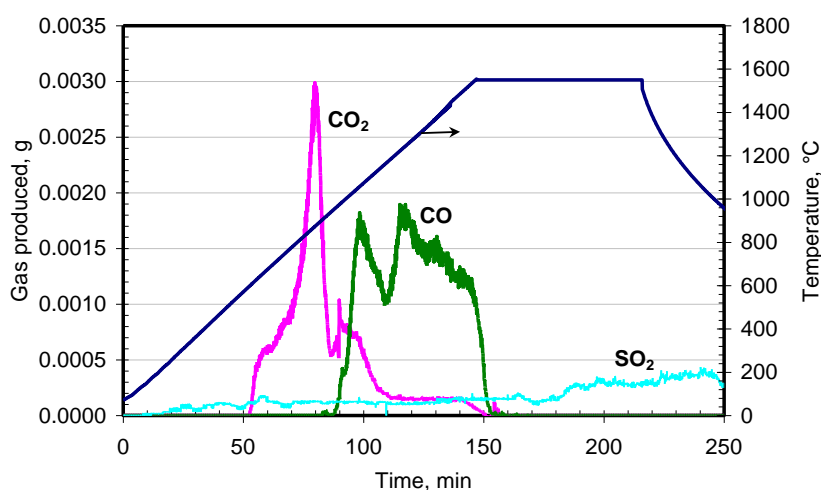


Figure 7: Off-gas analysis of the fly ash and BOF flue dust coarse fraction mixture with additive of SiO₂ – reduction with the residual carbon in the ash; 10°C/min under N₂ atmosphere, equilibrated at 1550°C

Table 2 shows the experimental conditions, the metal yield and composition of both metal and slag phases. Carbon content was analysed with LECO and SEM/EDS. It is demonstrated through laboratory scale experiments that ferrovanadium with about 20 wt% V content is obtained with the stoichiometric mixture without extra carbon addition, which has the advantages of using the waste based materials with high environmental benefit and resource saving. The major concern is the high carbon content in the alloy which will lead to the vanadium carbides formation, and relatively low content of vanadium in the alloy. The impurities in the formed alloy phase will need a further refining step, for instance, through oxidation refining. High recovery of vanadium from the fly ash needs further investigation.

Table 2: Ash smelting results in a vertical tube furnace at 1550°C for 2 hours in Ar.

Test	Charge, g			Slag, wt%						Metal, wt%		
	Fly ash	BOF-dust	SiO ₂	CaO	SiO ₂	MgO	FeO	VO	NiO	Fe	V	Ni
A-1	1.28	1.59	0.96	28.3	35.6	6.50	15.6	0.13	0.07	63.0	18.2	1.89
A-2	0.95	1.59	0.95	26.0	44.8	5.25	12.4	0.19	0.05	62.2	20.8	1.15
A-3	16.0	20.0	12.0	33.6	38.6	7.23	4.58	0.96	0.10	62.4	22.6	1.88

It proves that the high carbon content in the fly ash can be used as reductant for reduction of iron oxides in BOF flue dust and the vanadium oxides in the fly ash. An alloy with about 20 wt% V ferrovanadium is obtained at 1550°C, with a certain addition of silica for slag formation. On average about 30% of metal yield (calculated by the amount of metal produced divided by the total raw material input) was

obtained during smelting of the ash mixture with the fly ash to BOF flue dust (coarse fraction) in 4:5 in weight ratio, and vanadium recovery in metallic form has reached about 50%. To improve the metal recovery, selecting a proper slag forming agent may be essential.

The thermodynamic prediction indicates that sulfur in the fly ash can be removed from the system at temperatures below 1200°C, however, a lot of sulfur is found as CaS in the slag. Kinetic factors in sulfates decomposition may play an important role, which deserves further study. Efficient carbon control for a quality ferroalloy is thermodynamically possible, which is essential to reduce the potential for vanadium carbide formation during cooling. A recipe based processing can be a sustainable and economical option for waste management, if a market valuable metal product can be produced. The benefits incorporate both resource savings and better environmental conditions.

Summary and perspectives

Evolutions in technology have been taking place all the time along the production processes in the high temperature waste processing with the objectives of waste reduction, immobilisation and, moreover, resource recovery. Based on laboratory experiments, several examples have been described. It is clear that there are fundamentally new challenges, in particular with respect to secondary waste generation control and process efficiency.

- *Increasing pressure on the reduction of environmental impact.* Global warming gas generation is still one of the major problems in the energy intensive metallurgical industry. Innovative and revolutionary technology is highly needed for drastic reduction in energy consumption but not yet readily available.
- *Interdisciplinary research for the efficient waste management and resource recovery:* Investigation of the characteristics of broad secondary resource (the urban mines), and the exploration of the potential for a smarter processing route with the recipe-based concept are highly needed. Fundamental knowledge such as the phase diagrams is required for the slag compositions outside the known region of available phase diagrams, and new thermodynamic data are and will be very valuable. Innovative process control to minimise the risk of generating substantial secondary wastes, and strict control of volatile components are important aspects during high temperature waste processing. Under the present strategy of a low carbon economy, the energy consumption of the process will become a very important issue as well. Selection of a smarter technology is critical. The

concept of recipe-based combined waste processing technology can be a good option for the future waste management.

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