Thermochemical Treatment — Technologies for Recovery and Utilisation of Materials

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Abstract: The arc furnace technology is an ideally suited process for the treatment of hazardous and problematic waste. The operation conditions of the furnace can be adapted for optimal transformation of the waste material input into raw materials and usable products. The process can significantly reduce the impact of contaminated wastes and industrial residues, and enable material conversion and separation. Thus, the products of the process have various applications. The capability of the process is illustrated with three examples, the treatment of bottom ash and filter ash from waste incineration plants, of stainless steel slags and of chromium-containing residues from the refractory industry.

Key words: thermochemical treatment; materials separation; refractories; stainless steel

1　INTRODUCTION

Dumping of hazardous waste on landfills or in abandoned mines is not sustainable from an ecological, economical and political viewpoint. The environmental impact of hazardous wastes and residues from industrial processes such as fly ashes, filter cakes, cast sands, metallurgical slags, grinding debris and so on must be kept as low as possible by applying advanced material separation technologies that can also facilitate extensive recycling, re-use and re-utilisation. The use of industrial waste products as secondary raw materials in metallurgical processes and the processes for the production building materials or other useful materials is being evaluated.

Since the invention of the arc furnace principle by the French chemist Henri Moissan (1852~1907, Nobel Price 1906) in the 1890s[1], the arc furnace has reached broad application in the metallurgy and in the silicate industry, mainly as a heating and melting aggregate. In the Federal Institute for Materials Research the arc furnace technology is applied for thermochemical materials separation. Thermochemical processes are well suited for the treatment of waste materials enabling a recovery of useful elements and products. Thermochemical treatment comprises a variety of processes over a wide temperature range[2,3]: combustion and pyrolysis as well as partial oxidation, hydrogenation, hydrolysis, alcoholysis[4], special technologies and combinations of all these.

Treatment of waste materials in an arc furnace displays a special technology. Usually applied for scrap smelting or the production of high temperature materials[5], the furnace enables a separation of materials by applying reducing conditions and high temperatures.

2　ARC FURNACE PILOT PLANT SCALE INSTALLATION

BAM operates a closed AC-electric arc furnace (three carbon electrodes, 300 kW, capacity 100 kg/h charged in 25 kg portions) fitted with a handling system to transport contaminated materials and with systems for flue gas cleaning (bag filter, activated carbon filter, CO-afterburner) and a gas analysis system[6,7]. In this furnace the solid residues are melted and detoxified. The melt is poured into graphite moulds giving casting blocks of ~15 kg. The flue gas is quenched with excess air to T<120 ℃. Particles from re-sublimation are separated on a bag-filter from residual gases which are cleaned in two activated carbon filters. The gases are quantitatively analysed (CO, CO_2, O_2, NO_x, SO_2) and finally treated in a CO-afterburner, according to the German regulations for air emissions. A sketch of the BAM pilot plant scale installation is shown in Fig.1.

The electric arc furnace (melting vessel d~1 m) is the central aggregate of the installation. The carbon from the electrodes may partly react under special melting conditions (resistance melting or working with a short arc) with oxide components which appear in the input materials, leading to the formation of reduced components. If the velocity of the carbon particles is low or the distance between the electrodes and the melt is large enough (working with a long arc), carbon is oxidised to CO or CO_2 before it will be in contact with the melt and will almost lose its reducing potential.
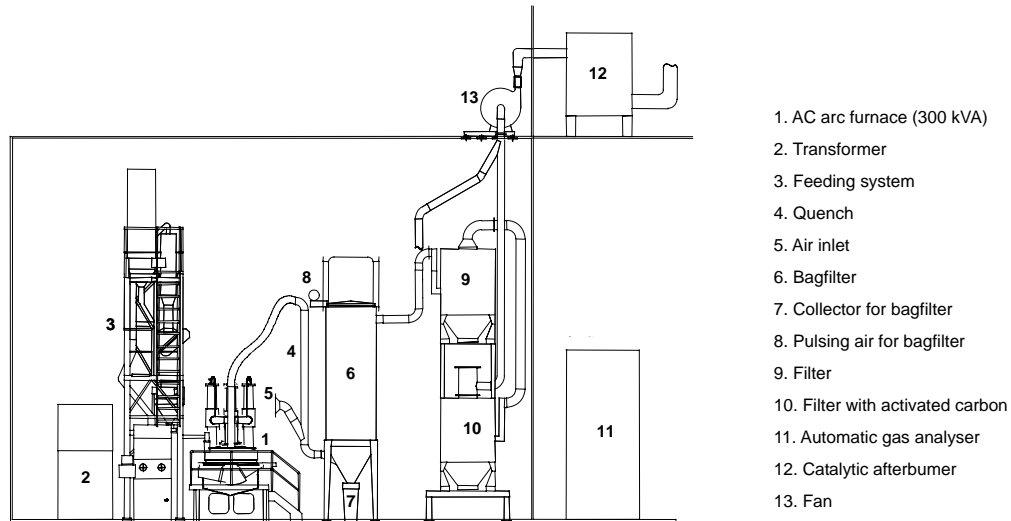
Fig.1 Sketch of BAM's pilot plant scale installation

1. AC arc furnace (300 kVA)
2. Transformer
3. Feeding system
4. Quench
5. Air inlet
6. Bagfilter
7. Collector for bagfilter
8. Pulsing air for bagfilter
9. Filter
10. Filter with activated carbon
11. Automatic gas analyser
12. Catalytic afterburner
13. Fan

An analysis of the free standard enthalpy ΔG of formation of possible system components is displayed in Fig.2. Here the values of ΔG are plotted versus the temperature. Reduction of the oxides by CO is thermodynamically feasible at temperatures higher than the temperature of intersection of the lines. That means that in the presence of carbon the stability of the oxides decreases in the following order: CaO, MgO, Al_2O_3, SiO_2, Cr_2O_3, Na_2O, ZnO, K_2O, FeO, CdO, NiO, PbO, Fe_2O_3, Cu_2O, CuO, HgO[2]. Above the intersection the dominant reaction is:

$$Me_mO_n+nC \rightarrow nCO+mMe \quad (Me \text{ for Al, Si, Cr, } \cdots). \quad (1)$$

Below the intersection the oxides are stable and the following reaction takes place:
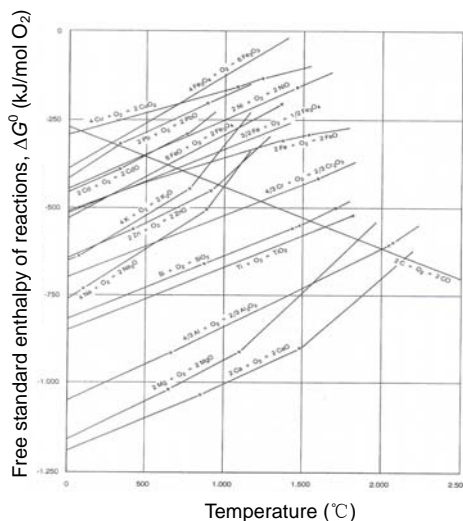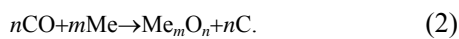
$$nCO+mMe \rightarrow Me_mO_n+nC. \quad (2)$$

Fig.2 Richardson–Jeffes diagram for some oxides (from Ref.[8])

3 TREATMENT OF FLY ASH FROM MSWI, REDMELT®

Municipal solid waste incineration (MSWI) is a proper treatment for household and industrial wastes. The volume is reduced by 90% (75%, by weight) and the energy content of the input can be used to generate heat and power. However, solid residues are formed during the incineration and the subsequent flue gas cleaning. From these residues the fly ash has the highest hazardous potential. Fly ash from MSWI is separated from the flue gas by cyclone, electrostatic precipitators or bag filters and is composed of Al, Ca, Mg and Si-oxides, alkali halogenides and sulfates. The ash contains considerable amounts of toxic heavy metals (copper, lead, zinc, cadmium) and traces of organic pollutants, e.g. dioxins and furnaces.

A promising approach for the transformation of fly ashes from MSWI and hazardous wastes into reusable useful materials is the separation of the heavy metals and salts from the oxides by a thermal treatment under reducing conditions in an electric arc furnace with the Redmelt® process[9]. Fig.3 displays an overview of the RedMelt® process.

The dry fly ash is fed from a silo of the handling system to the melting vessel of the electric arc furnace. Additives such as municipal solid waste incinerator bottom ash are added if required.

During the process the input material is thermally treated above its melting point which ensures thermal decomposition of the toxic organics. In the reducing atmosphere, zinc-, lead-, cadmium- and mercury-compounds are reduced and transferred to the

gas phase together with alkali chlorides. The metals are reoxidised during the cooling process in excess air and condensed together with the alkali chlorides, forming a

fine dust which is separated from the off-gas in a bag filter. This condensate can be utilised in the metals recycling industry.
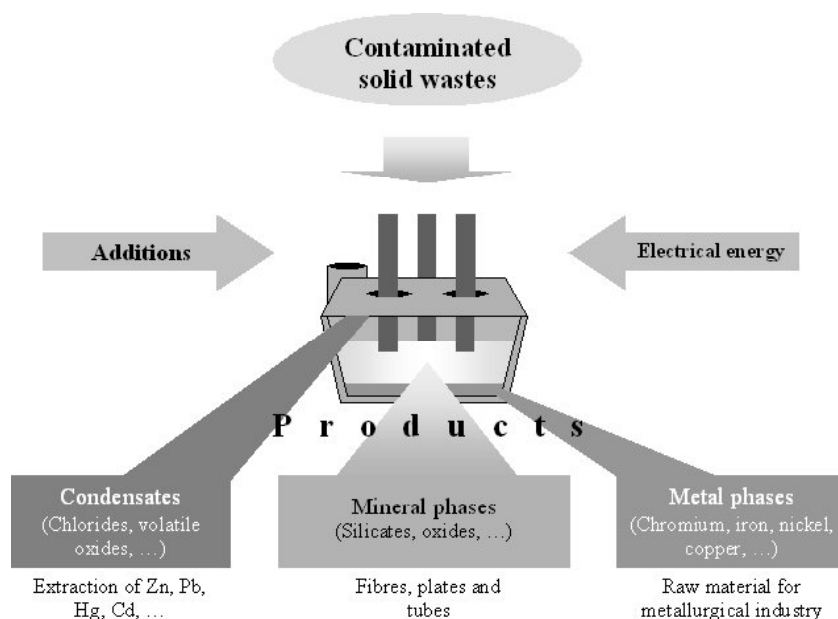

Fig.3 Process flow sheet for the thermochemical conversion of hazardous wastes

According to the Richardson–Jeffes diagram in Fig.2 the heavy metal oxides of Fe, Cu, Cr and Ni are also reduced. Due to their high density the metals sink down and are separated from the silicate phase. This bottom metal phase is alloy of iron, copper and some other metals and can be recycled in the copper industry. The remaining bulk material is in the form of an inert, vitrified silicate product. Possible applications for this silicate phase are mineral fibres, foam glass, tubes and plates, where the vitrified product will substitute the usual raw materials or glass–ceramics with enhanced physicochemical properties[10].

In Table 1 the chemical composition of MSWI fly ash is displayed together with the composition of solid output fractions of the process, silicate phase, metal phase and condensate. The off-gas behind the bag filter contains some SO_2 and CO_2 from the thermal decomposition of sulfates and carbonates in the furnace. The proportion of glass-forming elements in the silicate phase depends directly on the composition of the input material. The condensate consists substantially of enriched heavy metal oxides ZnO, PbO, CdO and alkali salts (NaCl, KCl).

The RedMelt® process can be also applied for treatment of other contaminated inorganic waste materials like used grinding and blasting materials, ashes from power plants and so on[11].

Table 1 Compositions of input (fly ash/bottom ash mixture) and the solid reaction products

Element	Content (%, ω)			
	Input	Product		
		Silicate phase	Metal phase	Condensate
Si	22.00	26.20	3.40	6.40
Al	5.50	6.80	0.20	0.50
Ca	9.00	10.60	0.60	0.80
Na	3.90	4.20	0.08	13.70
Mg	1.20	1.40	0.01	1.10
K	1.40	1.20	0.10	9.40
Fe	10.10	4.50	85.00	1.40
Cu	0.30	0.03	4.40	0.30
Cr	0.04	0.04	0.20	0.30
Ni	0.01	0.0006	0.3000	0.0010
Zn	0.60	0.09	0.08	14.00
Pb	0.20	0.01	<0.01	6.30
Cd	0.0040	<0.000007	<0.001	0.10
Hg	0.0001	<0.000003	<0.01	0.0020
C	2.00	<0.000003	0.30	n.d.
Cl	1.30	0.30	0.02	23.50
P	0.60	0.20	2.40	3.70
S	0.90	0.40	1.70	4.80

4   RECYCLING OF STAINLESS STEEL SLAGS

In the production of stainless steel a slag containing a residual metallic fraction is generated. In Europe 1 million tons per year of the slag are produced. The slag contains heavy metal oxides, namely chromium(III)-oxide (Cr_2O_3), which is formed during the decarburisation process and can not be prevented

completely. The main component of the slag is dicalcium silicate (Ca₂SiO₄, belite) which is of great importance as constituent in cement clinkers. In the stainless steel slag, however, the dicalcium silicate mainly occurs in a modification with no hydraulic properties and therefore it can not be used as a clinker substitute in the cement industry. Due to the amount of chromium and chromium compounds, the slag from stainless steel production exhibits a risk to the environment[12]. Therefore, the direct application of the slag as a building material or as a substitute in the cement industry is prohibited and it is only used partially in qualitative inferior applications[13,14].

In today's treatment of the stainless steel slag the metallic granules are partially removed manually or by magnetic or gravity separation methods from the slag[15,16]. The mineral-bound chromium (Cr_2O_3, 2%~4%) and smaller metallic particles remain in the slag. Without further treatment the loss of valuable raw materials currently can not be avoided.

The treatment of stainless steel slag in an arc furnace aims on a similar principle described above (RedMelt®) and enables a complete utilisation of the slag. In the molten state the metallic and mineral fractions are separated due to their difference in density. The metal droplets accumulate on the bottom of the melting bath, where they form a layer of metal alloy. Furthermore, heavy metal compounds are reduced almost completely to their elemental form by carbon from the graphite electrodes or other supplementary reducing agents and are transferred to the metal phase. Fig.4 shows the effectiveness of reduction with different melting conditions and with the addition of refinery coke (carbon) as reducing agent for this purpose. As seen, none of the arc melting operation mode is effective in reduction. The amount of Cr_2O_3 does only decrease slightly for both, long and short arc melting. Both operation modes cause a significant convection in the melting bath. While in arc melting the electrodes hang over the melt, only the emitted carbon from the hot burn spot reacts. Although the reducing impact of the emitted carbon is even higher than the strongest reducing agent due to its atomic state (quasi-*in statu nascendi*), its concentration and amount are restricted by the specific capacity of the electrodes. Because of the distance between the electrodes and the melt, high reactive carbon will be almost oxidised to carbon monoxide before it comes into contact with the molten mass. Even the addition of supplementary reducing agent to the melt has only a minor impact. This seems to be an effect of the re-oxidation of metallic particles due

to the relatively high convection in the arc melting operation modes. This assumption is supported by the increased Cr_2O_3 content compared with the source material when melting without additional reducing agent. The most effective operation mode is resistance melting. Here, the electrodes are in direct contact with the melting bath. The carbon is effective on the electrodes surface only, but the amount is significantly higher than that in arc melting modes. Furthermore, the convection of the melting bath is lower than that in the arc melting modes. This enables a fast separation of the metal droplets and re-oxidation takes place at lower rates than those with long or short arc. The reduction efficiency can be strongly enhanced by addition of supplementary reducing agents like carbon, Si, FeSi or Al. As seen in Fig.4, a simple addition of refinery coke (carbon) to the melt reduces the content of chromium oxide by 80%. A further enhancement is possible, when the additional reducing agent is injected via a blowing device. This enlarges the effective reaction surface, and the reducing agent is distributed by additional convection. Due to the short injection time, the chance for re-oxidation reactions of the metallic droplets is low. The injection is essential for reducing agents with higher density, like SiC or FeSi. If such compounds are added as usual, they will sink down to the bottom of the reaction vessel, where they form an alloy with the metallic phase and almost lose the reducing potential.
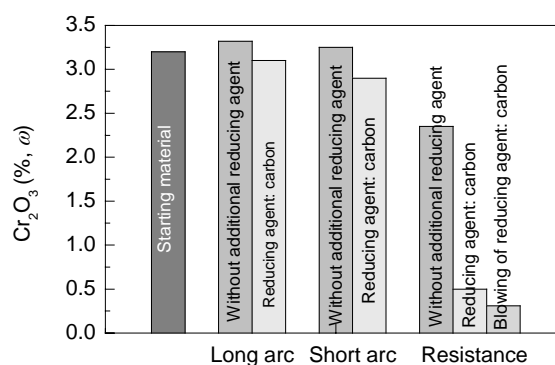

Fig.4 Effects of the electrical operation mode and the addition of reducing agents on the chromium content of the slag (Refinery coke was added in a concentration of 0.8% as reducing agent)

Some of the reducing agents will not only act as reducing agents but also influence the composition and the properties of the mineral fraction of the slag. For example the Al_2O_3, forming according to Eq.(3), becomes part of the slag and the formation of alumosilicates is possible.

$$Cr_2O_3+2Al \rightarrow 2Cr+Al_2O_3. \qquad (3)$$
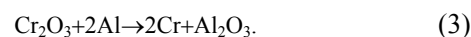
For the separation of both phases the mineral phase will be decanted and cooled down. Naturally an irreversible phase transition from α/α'- to γ-Ca_2SiO_4 takes place with the metastable β-Ca_2SiO_4 intermediate at approximately 400 ℃. Due to an increase in volume by approximately 10% during the phase transition from β- to γ-Ca_2SiO_4 the microstructure is destroyed and the mineral phase will disintegrate into a fine powder, which prevents an utilisation as construction material. In addition, the γ-Ca_2SiO_4 has no hydraulic properties and therefore no use as a clinker substitute in the cement industry. For this reason the β- to γ-transition must be avoided by suitable measures (splat cooling, chemical stabilisation of the metastable phase).

The generated chromium-rich alloy can be used directly as raw material in the stainless steel production. Since the chromium content in the slag is significantly decreased, an utilisation of the mineral phase as building material will be possible. Consequently the described way of the thermochemical treatment in an arc furnace enables a complete recycling of the stainless steel slag and makes sense economically and ecologically[17].

5　RECYCLING OF CHROMIUM-CONTAINING REFRACTORY MATERIALS

Chromium-containing materials are the most refractories suitable for processes at high temperatures and highly corrosive environments. However, due to the risk of mobilizing toxic hexavalent chromium ions they are also the most problematic in regard to the end-of-life strategy. Wastes of chromium-containing refractories are regarded as hazardous waste and require either special treatment or safe disposal. Until now an alternative to refractory chromium oxide with high resistivity against corrosion has not been found. A treatment of spent refractories favorably includes the treatment of residues from furnace and refractory construction and installation, i.e., sludge from sawing, grinding and polishing. According to implemented companies, the amount of the sludge alone is approximately 500 t/a in Germany.

The refractories are produced from corundum and chromium oxide mixtures which exhibit a melting point higher than 2000 ℃. The content of Cr_2O_3 in refractories for high-end application is around 90%. Chromium oxide in waste refractories is recycled by the formation of mixed crystals of Cr_2O_3 and Al_2O_3 (escolaite-corundum). The Cr_2O_3-rich waste and clay (Al_2O_3) are melted in the arc furnace. The resulting product can be used as raw materials for new refractories with high resistivity against corrosion. It can be expected that the mixed crystals show at least equal, if not better, refractory properties to the conventional, two-phase refractory mixtures of Cr_2O_3 and Al_2O_3.

As described above the reducing operating conditions can be used to remove heavy metals from the mixtures fed to the furnace. In the recycling of spent refractories and chromium-containing sludge, reduction to the elemental form is, contrary to the recycling of stainless steel slags, not desired. At elevated temperatures, the reduction of Cr_2O_3 and even of SiO_2 (to SiO which is a stronger reducing agent than CO) is possible, as seen from the thermodynamic data in Fig.2. Therefore the reaction conditions have to be chosen carefully to avoid reduction of chromium to its elemental form. By melting with long arc most of the emitted carbon from the electrodes will be oxidised to CO before it is in contact with the melted mass. Because the formed CO is removed from the furnace by the off-gas system, it will not act as reducing agent in the treatment. Under such "non-reducing" conditions the formation of elemental chromium can be almost inhibited.

The formation of the chromium-corundum mixed crystals is confirmed by the X-ray patterns shown in Fig.5. The general shifts in the 2θ angles of the peaks in the XRD patterns are indicated by vertical lines at three peak positions. The replacement of chromium on Al-lattice sites results in slight deformations of the corundum-structure implied by decreasing intensities and increasing full width-half maximum (FWHM) in the XRD patterns with higher amounts of chromium.
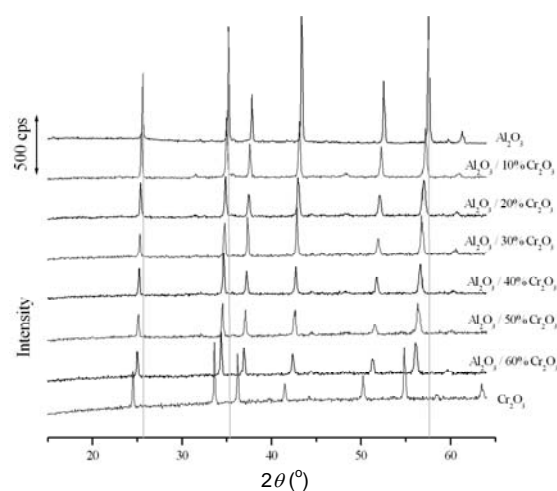

Fig.5 X-ray patterns of chromium-corundum mixed crystals with Cr_2O_3 concentrations from 10% to 60% (3 peak positions are indicated to show the general shift in peak positions observed)

Due to their low amounts and their partial amorphous state (vitreous phases), other phases are not detectable by powder diffraction, but can be observed by microscopic methods. These phases are a result of the thermochemical treatment and from residual matter in the waste material (glassy attachments), and are found in all escolaite-corundum products.

Tests for corrosivity with the melting products in glass melts showed equal or better results than conventional refractories with comparable compositions[18].

6 CONCLUSIONS

The treatment of hazardous and problematic inorganic wastes in an electrical AC arc furnace exhibits a good opportunity for the recovery of valuable resources. Various applications have already been tested successfully: treatment of MSWI residues (bottom ash and fly ash), treatment of residues from iron and steel industry, and treatment of inorganic waste, such as chromium-containing refractories. The operating conditions of the arc furnace can be adjusted in such a way that the waste input can be transformed to usable products and raw materials. Harmful or toxic components can be converted into harmless compounds. This helps to lower the environmental impact and offers a source for valuable raw materials.

For the operation of the arc furnace, electrical energy is needed. Most of the conventional processes for the production of silicate products and refractories as well as the extraction of raw materials are high temperature processes with a high-energy demand. Therefore the consumption of electricity is justified. The thermochemical treatment of residues in an AC arc furnace is a technically mature process and a full scale application is desirable.

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