CHARACTERIZATION OF STEEL MILL ELECTRIC-ARC FURNACE DUST

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Abstract: - EAF dust is a complex material consisting mostly of metal oxides. Since electric arc furnaces typically rely on scrap metal for their charge and the composition of the dust is directly associated with the chemistry of the metallic charge used, increased use of galvanized steel to manufacture automobile bodies and paneling has increased the zinc content in the dust over the years. When galvanized steel scrap is melted in a steel making furnace, most of the zinc vaporizes and ends up in the dust as zinc oxide and zinc ferrite. In addition, trace quantities of precious metals such as gold are also found in EAFD.In order to make a complete characterization of electric-arc furnace (EAF) dust, as hazardous industrial waste, and to solve its permanent disposal and/or recovery, bearing in mind both the volumes formed in the steel industry and experiences of developed industrial countries, a study of its properties was undertaken.
For this purpose, samples of EAF dust, taken from the regular production process in more Integrated iron and steel works were subjected to a series of tests. The chemical composition of EAF dust samples was investigated by means of a several different analytical methods. The results from the chemical analysis show that the approximate order of abundance of major elements in EAF dusts is as follows: Fe, Zn, Mn, Ca, Mg, Si, Pb, S, Cr, Cu, Al, C, Ni, Cd, As and Hg. Granular-metric composition of single samples was determined by applying sieve separation. Scanning electron micro-structural examination of EAF dust microstructure was performed and results indicated that all twelve EAF dusts were composed of solid spherical agglomerates with Fe, Zn, Pb, O, Si and Ca as the principal element.
The investigation of grain morphology and the mineralogical composition of EAF dust were taken by combination of high resolution Auger electron spectroscopy (HR AES), X-ray photoelectron spectroscopy (XPS) and X-ray powder diffraction analysis. The analysis of XPS-spectra determined the presence of zinc in the form of ZnO phase and the presence of lead in the form of PbO phase, i.e. $PbSO_3$/$PbSO_4$ forms. The results of the X-ray diffraction phase analysis show that the basis of the examined EAF dust samples is made of a mixture of metal oxides, silicates and sulphates.

Key-Words: - steel industry, EAF dust, metal oxides, water, hazardous industrial waste, environment

1 Introduction

Steel production by electric-arc furnace (EAF) technology has been increasing in importance over the past 20 years at the expense of traditional open hearth and basic oxygen converter technology, reaching an estimated 33.4% world share in 1999. This trend looks set to continue, and it is expected, for example, that more than 50% of the steel produced in the USA will be by this route within the next few years (1999: 46.2%). When steel is produced using an electric arc furnace, about 15 - 20 kg of dust is formed per tonne of steel. This dust is considered as a toxic waste due to its content of heavy metals. It is estimated that the world-wide total production of EAF dust could be as high as several million tonnes, all of which must be treated, recycled or land-filled. The EAF dust forms as a result of volatile metals, like zinc and lead, passing into the vapour phase at the operating temperature of the furnace and being oxidized and cooled in the extractive air flow. These metals are therefore found in the resulting dust both as free oxides and in the form of composite structures with iron oxides. These latter compounds are notably of the spinel type, MFe_{2O4} (M = Fe, Zn, Ni, Mn or Cd). Overall, EAF dusts contain major elements of the type iron, zinc, calcium and silicon (these last two from the degradation of the refractories) in the form of simple or mixed oxides, and minor elements like copper, manganese, chromium, cadmium and lead present in the scrap iron raw material or introduced as additives. The dusts also generally contain significant amounts of chlorides [1].

2 Problem Formulation

EAF (electric arc furnace) dust is formed under minimill steelmaking operations due to the high processing temperature (around 1600 °C). Certain metals such as Zn, Pb, Cd, Na, Mn and Fe are volatilized and oxidized, then condensed or mechanically carried over and finally collected as appeared as dust form. Because it contains water leachable heavy metals such as lead, chromium and cadmium, EAF dust was categorized as hazardous waste K061 under EPA regulation in 1980 [2]. Management of EAF dust becomes a major economic minimill steelmakers due to the environmental concern.

The morphology of the EAF dust was observed from SEM analysis. As shown in Figure 1, the dust generally contains very tiny (less than 2 µm) spheroids, some of which agglomerate into relative large particles (10-100 µm). Figure 1(a) and (b) illustrate composition variations of particles in different sizes. The small particles mainly consist of $ZnFe_2O_4$ and Fe_3O_4, which fill about 80-90% of the whole dusts. Medium size particles are metal oxides or silicates. The big particles are mostly Fe-enriched silicates or oxides and there are fine oxides particles attached on them. In general, EAF dust contains mainly of $ZnFe_2O_4$, Fe_3O_4, FeO, ZnO, minor amount KCl, Fe-Al-Ca-Zn-Mg oxides, and trace amount of Fe_2O_3 and various silicates. However, nearly none of these compounds was found to be pure in composition. Element substitution for each other is common in these compounds [3]. For example, in a typical $ZnFe_2O_4$ particle, 1.33 % Ca, 1.2 % Mg, 1.78% Mn was observed to substitute for Zn and Fe. These substitutions indicate the complexity of the dust compositions.

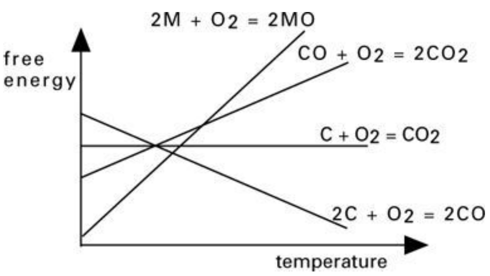

Fig. 2

Contaminants in recycling molten metal ‘solutions’ are removed using the principles of oxidation and reduction, which can be described graphically on the Ellingham Diagram.

The investigation of grain morphology and the mineralogical composition of EAF dust were taken by combination of high resolution Auger electron spectroscopy (HR AES), X-ray photoelectron spectroscopy (XPS) and X-ray powder diffraction analysis. The analysis of XPS-spectra determined the presence of zinc in the form of ZnO phase and the presence of lead in the form of PbO phase, i.e. $PbSO_3$/$PbSO_4$ forms.

The results of the X-ray diffraction phase analysis show that the basis of the examined EAF dust samples is made of a mixture of metal oxides, silicates and sulphates.

It has been done more analyses of EAF dust to point out metals content in more Integrated iron and steel work.

All concerns are focused on iron and zinc since they are the most abundant valuable elements in the dust. [4].

Fe %	**P %**	**MnO %**	**SiO_2 %**
1	2	3	4
14.0	0.05	1.05	2.50
23.0	0.04	3.60	2.19
Cr_2O_3 %	**Zn %**	**Na %**	**TiO_2 %**
8	9	10	11
0.14	5.14	0.53	0.08
0.25	17.40	1.80	0.05
Pb %	**Al_2O_3 %**	**CaO %**	**MgO %**
15	5	6	7
1.03	0.79	52.70	3.49
2.91	0.66	22.10	1.56
	K %	**C %**	**Cd %**
	12	13	14
	0.32	5.37	016
	0.17	0.61	0.04

Table 1 Analysis of carbon Steel EAF Dust Sample #1 Sample2

Fe_2O_3 %	**MnO %**	**SiO_2 %**
42.5	6.3	2.6
Cr_2O_3 %	**ZnO %**	**Na_2O %**
15.1	6.5	1.3
MgO %	**Al_2O_3 %**	**CaO %**
4.6	0.6	5.9
Ni_2O_3	**K_2O %**	**PbO %**
5.7	1.4	1.1

Table 2 Analysis of stainless steel EAF

dust

Register No.	Specimen marking	SiO_2
54	Mold powders	30.15
55	Tundish slag	36.55
56	1 Electrofilter powders	7.08
57	2 Electrofilter powders	4.63
		MgO
54	Mold powders	1.14
55	Tundish slag	7.59
56	1 Electrofilter powders	2.79
57	2 Electrofilter powders	2.40
TiO_2	**CaO**	**Na_2O**
0.28	19.29	9.50
0.18	10.14	0.23
0.23	9.04	1.61
0.08	3.67	3.66
PC	Cr_2O_3	C
29.95	-	-
-	0.41	-
-	0.52	1.80
5.06	-	1.02
Al_2O_3	**Fe_2O_3**	
5.79	1.84	
3.35	7.25	
3.16	45.40	
0.67	35.09	
P_2O_5	S	
0.12	0.22	
-	-	
0.44	0.93-	
0.35	1.35	
K_2O	**MnO**	
1.05	0.02	
0.34	34.34	
0.82	3.32	
2.40	2.97	
ZnO	**PbO**	
-	-	
-	-	
19.50	-	
31.31	4.75	

Table 3 XRF analysis of powders (m/m)%

Specimen marking			**Cd**	**As**
1			0.03	0.010
2			0.02	0.011
3			0.03	0.010
4			0.03	0.010
Cr	**Cu**		**Mn**	**Pb**
0.61	0.23		2.74	0.31
0.64	0.21		2.71	0.29
0.63	0.22		2.70	0.29
0.61	0.21		2.72	0.30
Co	**Ni**	**As**	**Co**	**Ni**
0.006	0.92	0.010	0.006	0.92
0.007	0.95	0.011	0.007	0.95
0.007	0.95	0.010	0.007	0.95
0.006	0.95	0.010	0.006	0.95
Zn		**Pb**		**Zn**
3.13		0.31		3.13
2.88		0.29		2.88
2.91		0.29		2.91
3.09		0.30		3.09

Table 4 EBT filter dust (ladle refining furnace)

Specimen marking	**Cd %**	**As %**	**Co**
1	0.1	0.011	0.005
2	0.1	0.011	0.005
3	0.09	0.012	0.005
4	0.09	0.012	0.005
Cr	**Cu**	**Mn**	**Pb**
0.27	0.35	3.33	0.26
0.28	0.35	3.29	0.24
0.28	0.34	3.41	0.27
0.27	0.35	3.34	0.23
Ni	**V**		
0.09	Trace		
0.08	Trace		
0.10	Absence		
0.10	Absence		

Table 5 EAF furnace electrofiter dust

The dust has a chemical composition depending on the steel grade that is elaborated, varying during the making process.This is seen in Table 6:

Element	**Romania (unalloyed steel)**	**USA**	**Germany (unalloyed steel)**
Fe total	34.57 - 42. 28	16.4 – 38.6	21.6 – 43.6
Si	2.34 – 2.96	0.9 – 4.2	0.9 – 1.7
Al	0.67 – 6.42	0.5 – 6.9	0.1 -1.5
Ca	3.79 – 7.61	2.6 – 15.7	6.6 – 14.5
Mg	1.67 – 2.70	1.2 – 9.0	1.0 – 4.5
Mn	3.35 – 4.16	2.3 – 9.3	0.9 – 4.8
P	0.075 – 0.12	<1.0	0.1- 0.5
S	0.59 – 2.16	< 1.0	0.3 – 1.1
Zn	3.13 – 20.0	<35.3	5.8 – 26.2
Cr	0.18 – 0.26	<8.2	< 0.1
Ni	Data missing	<2.4	Data missing
Pb	0.30 – 3.11	<3.7	1.3 – 5.0

**) elements performed are found like oxides*

Table 6 Comparative analyses of EAF dust(%)

During the steel making process, approximately two percent of the raw materials added to the furnace are converted into bag house dust. It has been estimated that 0.5 to 0.6 million tons (USA) of electric arc furnace dust (EAFD) containing zinc and lead.

Electric Arc Furnace Dust (EAFD):

. Airborne dust generated in the steel manufacturing process when metal scrap is electrically melted.
. Classified as hazardous waste because of its heavy metal content mainly Zn,Pb,Cr and Cd.
. It is listed in the European Waste Catalogue (EWC, 2002) as a hazardous waste with the code of 10 02 07*. (*solid wastes from gas treatment containing dangerous substances).
. The most common phases found in the EAFD are; franklinite(ZnFe2o4),magnetite(Fe3O4)and zincite(ZnO)

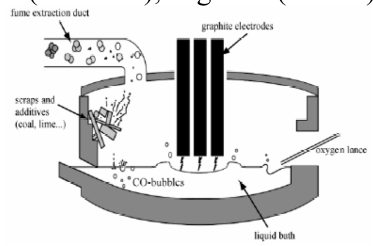

Fig. 4 Source: Guézennes et al./Powder Technology 157 (2005)-2-11

Oxide	PA_1(%, dry wt.)	PA_2(%, dry wt.)
ZnO	48.2	40.2
Fe_2O_3	29.2	36.0
CaO	4.67	6.22
MgO	4.06	5.56
MnO	5.85	3.77
SiO_2	1.74	1.96
SO_3	-	1.66
PbO	1.29	1.30
Cl	0.48	0.90
K_2O	0.62	0.80
Cr_2O_3	1.10	0.67
Al_2O_3	0.15	0.32
CuO	0.21	0.21
P_2O_5	-	0.14

PA_1, PA_2Sample [5]

Table 7 Oxide composition EAFD waste determined by XRF

3 Problem Solution

There are four common processes to treat EAF dust. Stabilization/fixation processes are used to encapsulate toxic metals such as lead and cadmium such that the dust will not be judged as hazardous in TCLP tests. The stabilized/fixed waste is disposed in commercial non-Title C landfills after being delisted. This process is widely practiced. However, with this method, there is no metal recovery.

Acid based extraction processes can be used to treat EAF dust to dissolve metals of interest. Since the inherent pH of a dust suspension is greater than 11, excessive amounts of acid would be required in this process. Thus, acid based extractions of EAF dust are not readily commercialized.

Pyrometallurgical processes are also commonly used to remove lead and zinc from EAF dust by fuming and then condensing the metals in relatively pure form. This technology is practiced in the United States and Mexico. The residual waste solid is delisted and available for use in roadbeds and can be disposed in a landfill. However, with hydrometallurgical processes, there is no recycle of iron to the EAF process. In addition, small particles of the lead or lead oxide in the vapor stream can be difficult to remove entirely. Thus, one concern with this process is the contamination of neighboring areas due to lead fall out.[5]

Most of the metals present in the dust, such as iron, are present in several valence states, which additionally complicates the development of suitable processes for the treatment of EAF dust. For example, iron is present as metallic form and as metal oxides of various oxidation states. The chemical complexity of the dust is enhanced by the amphoteric nature of these metals, the reducing or oxidizing conditions in the furnace and the presence of large quantities of metal oxides such as calcium oxide and magnesium oxide. These alkaline earth metal oxides also make the EAF dust suspensions highly alkaline.

Finally, caustic based processes in which the leaching and dissolving steps employ simple chemistry that takes advantage of the amphoteric nature of zinc, lead, tin, arsenic, selenium and aluminum and the basic conditions provided by the calcium oxide [6].

4 Conclusion

EAF dust cannot be simply disposed of. EAF dust fails environmental tests due to the presence of one or more of metals such as lead, cadmium, chromium and occasionally selenium at levels in excess of the regulatory limit. Thus, increasing disposal costs for this listed waste and more restrictive environmental legislation have led to the search for economically viable ways to recycle dust back into the process.

Due to its zinc and lead contents, steelmaking dust belongs to technological wastes of considerable environmental and human noxiousness, but, above all, it is a metal-bearing material that could be reused.

Exposure to dusts or fumes from some metals including zinc, manganese, chromium, cobalt and copper can produce a condition known as metal fume fever. Zinc poisoning can cause anemia, lethargy and dizziness. Early signs of manganese poisoning are sluggishness, loss of appetite, sleepiness, weakness in the legs, uncontrollable laughter, hallucinations, delusions, spastic or slow gait, speech impairment, aggressiveness, tremor, mask-like faces, and clumsy movements. May also result in CNS effects, anemia and lung damage.

Dust from EAF is rich in iron oxide, lead, zinc and other metals. Although attempts have been made to reclaim the iron oxide from the dust, dust containing lead and zinc cannot be readily recycled into the steel making processes. Thus, a need exists for extracting the lead and zinc from the EAF dust in order recycle the iron back into the process. In addition, the zinc and precious metals extracted from the process can be then sold commercially.

Eliminate hazardous waste through recycling, a superior alternative to the short and long-term issues associated with land-filling.

Successful recycle of the valuable metals (iron, zinc, and lead) present in the dust will result in resource conservation while simultaneously reducing the disposal problems.

References:

[1] Tahir Sofilić Alenka Rastovčan-Mioč, Štefica Cerjan-Stefanović, Vjera Novosel-Radović and Monika Jenko, Željezara Sisak Ltd., Božidara Adžije 19, 44000, Sisak, Croatia

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[2] Sofilic, T., Rastovcan-Mioc, A., Cerjan-Stefanovic, Š., Novosel-Radovic, V., and Jenko, M., 2004, “Characterization of steel mill electric-arc furnace dust.” *J. Hazard. Mater.,* Vol. 109, pp. 59-70.

[3]. Chen, T. T., Dutrizac, J. E., and Owens, D. R., 1998, “*Mineralogical characterization of EAF dusts from plain carbon steel and stainless steel operations*.” *Waste Process. Recycl. III*, pp. 511-525.

[4]. Xiang Sun, Jiann-Yang Hwang*, Xiaodi Huang, and Bowen Li, Microwave Heating *Department of Materials Science and Engineering Michigan Technological University, MI 49931 Journal of Minerals & Materials Characterization & Engineering*, Vol. 8, No.4, pp 249-259, 2009.

[5] Ignacio Fern´andez-Olmo *, Cristina Lasa, Angel Irabien, *Modeling of zinc solubility in stabilized/solidified electric arc furnace dust,* Departamento Ingenier´ýa Qu´ýmica y Qu´ýmica Inorg´anica, Universidad de Cantabria, Avda Los Castros s/n 39005, Santander, Spain,2007

[6]. *Process for hydrometallurgical treatment of electric arc furnace dust*, Related Applications,This application claims priority from U.S. Provisional Patent Application Serial No. 60/650,014 filed February 4, 2005.