LEVELS OF PCDD/DFs IN SOLID WASTES FROM AN ABANDONED COPPER MILL

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Introduction

The dioxin and furan inventories published by the United Nation Environment Programme in 1999 indicate that the manufacturing processes of non-iron metals, such as the primary and secondary recovery plants of copper, aluminum, zinc, and lead are one of the major sources of PCDD/DFs emissions[1]. A Japanese report published in 1999 from a review conference to control dioxin emissions estimated that the amount of PCDD/DFs emissions from the primary manufacturing process of copper industry was 4.0g-TEQ/year[2]. The release of PCDD/DFs from the copper metal process to land was 24g-TEQ/year in the United Kingdom[3]. The copper metal refinery process I s known to produce PCDD/DFs, and it is regarded one of the major sources of PCDD/DFs emissions.

Solid wastes were found in an abandoned copper mill in Taiwan. These wastes include waste slag, crude copper, sludge and so forth. This copper mill was suspected being contaminated with PCDD/DFs. The revision of the governmental regulations (i.e. the promulgation of the Identification Standards of the Hazardous Industrial Wastes by the Government of the Republic of China on March 7, 2001, the leaching standard of the Toxicity Characteristic Leaching Procedure (TCLP) of 2,3,7,8-TCDD is 0.001mg/L) and the apparent contamination by these wastes, a survey to investigate the levels of PCDD/DFs in solid wastes from this abandoned copper mill is, therefore, carried out.

This copper mill used to produce the electrolysis copper with 99.99% purity with an annual yield of 50,000 metric tons. The by-products include sulfuric acid, gold, and silver and so forth. The refining process includes the purchase of foreign raw material of copper (enargite, $3CuS \cdot As_2S_5$), followed by the process of baking, melting, blowing, refinery to produce the anodic copper, and finally through the electrolysis to produce the electrolysis copper. Figure 1 shows the flow diagram for generating products and wastes by this copper mill's manufacturing process.

Methods and Materials

The locations and characteristics of the potentially contaminated areas in this copper mill are depicted in Table 1. We carried out the preliminary sampling and analysis by a large scale and shallow layer (0-15 cm) method. That is if the solid waste is homogeneously distributed, the sampling points were at an equal-distance net. However, if the solid waste is heterogeneously distributed, the sampling points were randomly selected from the sampling area. Randomly selected samples with similar matrix or characteristics were mixed together to form an assembled

sample. The relevant sampling information, the characteristics of the samples, and the concentrations of PCDD/DFs are depicted in Table 2. The analysis method follows USEPA Method 1613 Revision B "Tetra-Through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS". Samples were analyzed using a HP5890/Micromass Autospec Ultima at a mass resolution above 10000, running with a 60m x 0.25mm x 0.25um DB-5MS column. The results are expressed using I-TEF in dry material (d.m).

Results and Discussion

The levels of PCDD/DFs in samples from the abandoned copper mill are shown in the last column of Table 2. The concentrations range between 0.004~6.158 pg-TEQ/g, indicating the presence of trace amounts of PCDD/DFs in every solid waste. Several solid wastes with different matrix designated as samples G~J were collected from Waste area (#5). The corresponding levels of PCDD/DFs are 0.290, 0.046, 0.004, and 6.158pg-TEQ/g, respectively. The influence of the heterogeneity of the sampling area upon the levels of PCDD/DFs in the samples is apparent.

The levels of PCDD/DFs in samples with similar matrix but collected from different sampling area are shown in Table 3. This copper mill used crude copper, lime, and crude silicon as the raw material. The crude copper was the dominant one. The crude copper contained higher concentrations of PCDD/DFs, ranging from 0.489 to 0.992pg-TEQ/g. The slag that is over 60% of the total wastes has relatively lower levels of PCDD/DFs, ranging from 0.021 to 0.147pg-TEQ/g. The sample B, C, and L collected from the sludge of the wastewater treatment plant had higher levels of PCDD/DFs, ranging from 1.026 to 3.449 pg-TEQ/g. We attributed this phenomenon to the transfer of the PCDD/DFs in the particular phase of the flue gas, to the effluent discharge from the air pollution control device, and finally to the sludge of the wastewater treatment plant.

In conclusion, trace amounts of PCDD/DFs were found in solid samples from the abandoned copper mill. The measured levels are within the typical range found in EU member states, i.e. <1 ~ 100 ng I-TEQ/kg d.m for soil and <1 ~ 200 ng I-TEQ/kg d.m for sewage sludge[4]. The preliminary results release the public from the speculation about PCDD/DFs contaminations in this abandoned copper mill.

References

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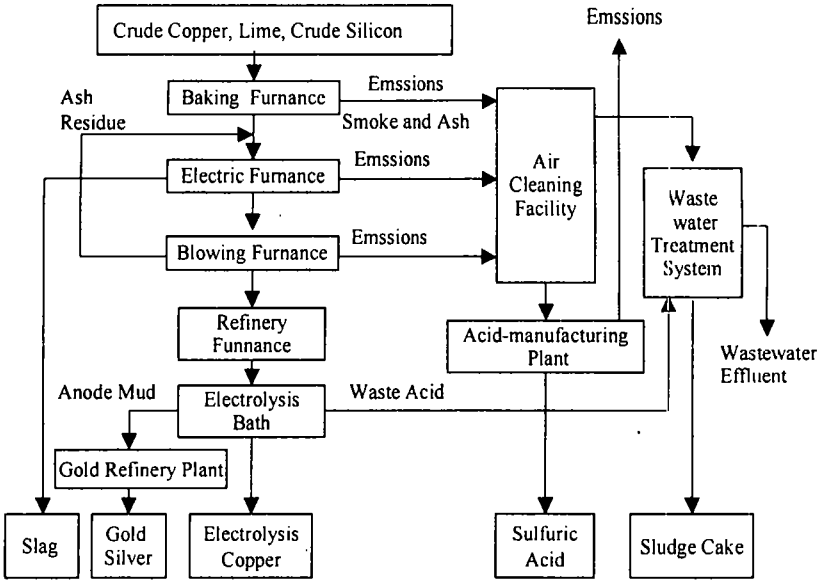

Figure 1. Flow diagram of generating products and wastes for the copper mill

Table 1. The locations and characteristics of the potentially contaminated areas in the copper mill

Area number (#)	Location	Length (m)	Width (m)	Characteristic
1	Original handling system for the loading of sulfuric acid	-	-	The area of man-made land which contain waste cables and general wastes.
2	The waste area of the ferric sulfide on the back of sulfuric acid tank	28	40	Wastes mixed with on-site rocks and soil , the wastes of construction materials are on the lower layer; some wastes had color similar to that of the crude copper.
3	The waste area of the wastes of construction materials is about 20 meters away from the back of the waste area of ferric sulfide mentioned above	22	24	Wastes mixed with on-site rocks and soil together.
4	On the upper back side of the copper mill, areas around the wall, three kinds of the areas	25 25 20	10 20 20	The area for piling slag; the distribution of the waste surfaces is rather homogeneous.
5	The storerooms for raw materials, crude copper, lime and crude silicon and their surroundings	6	6	The area for piling the waste of raw materials; the distribution of the wastes in this area is heterogeneous.
6	A storage tank under the cooling tower, it is currently used as the storage tank for crude copper	25	7	The area of the mixture of on-site rocks, the waste of construction materials and soil; the distribution of the wastes in this area is heterogeneous.
7	The area for electrolysis bath, it is currently used as the storage tank for crude copper	60	12	The area of the mixture of on-site rocks and soil; the distribution of the wastes in this area is heterogeneous; some wastes had color similar to that of the crude copper.

Table 2 The sampling points of the wastes in each area, the number of the mixing samples, the characteristic descriptions of the samples and the levels of PCDD/DFs

Area Number (Sample Number)	The sampling points of wastes	The mixing sample numbers	Characteristic descriptions of samples	Levels (pg-TEQ/g-d.m)
1(A)	3	1	Lumps with soil-like black and brown color	2.047
2(B)	6	1	Lumps with soil-like yellow and green colors	1.122
3(C)	2	1	Lumps with soil-like yellow colors	3.499
4(D)	10	1	Slag, granular, black and brown colors mixed	0.147
4(E)	30	1	Slag, granular, black and brown colors mixed	0.021
4(F)	30	1	Slag, granular, black and brown colors mixed	0.120
5(G)	1	1	Crude silicon	0.290
5(H)	1	1	Green crystals	0.046
5(I)	1	1	White lime stone residues	0.004
5(J)	3	1	Red and black materials from the surface layer of soil	6.158
6(K)	5	1	Crude copper	0.992
7(L)	3	1	Lumps with soil-like yellow color	1.026
7(M)	7	1	Crude copper	0.489

Note 1. The toxic equivalent is assigned "0" when the concentrations of PCDD/DFs are Non-detected (N.D.).

Note 2. The levels of PCDD/DFs are represented as I-TEF(1988).

Table 3 The levels of PCDD/DFs in samples with similar matrix but collected from different sampling area

Matrix	Sample number	Matrix characteristics	Levels (pg-TEQ/g-d.m)
Raw materials	G	Crude silicon	0.290
	I	White lime stone residue	0.004
	K	Crude copper	0.972
	M	Crude copper	0.489
Wastes from electric furnace	D	Slag	0.147
	E	Slag	0.021
	F	Slag	0.120
Sludge from wastewater treatment plant	B	Lumps with soil-like yellow and green colors	1.122
	C	Lumps with soil-like yellow colors	3.449
	L	Lumps with soil-like yellow colors	1.026
Other wastes	A	Lumps with black and brown colors	2.047
	H	Green crystals	0.046
	J	Red and black materials from the surface layer	6.158