

Conference Paper

Physical and Chemical Fundamentals and Technical Solutions for Recovery of Non-ferrous and Rare Metals from Industrial Wastes

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Abstract

The increasing demand for zinc and a range of zinc-related metals (for example: lead; indium; tin; cadmium; and copper) in the Russian Federation cannot be satisfied by the existing production plants due to the lack of raw materials. At the same time, ferrous and non-ferrous metallurgy and the chemical industry have accumulated hundreds of millions of tons of zinc wastes (falling into the hazard categories 2 to 4), the processing of which could not only make up the raw material base, but also improve the environmental situation. In the world, over 85% of ferrous dust is recycled using the Waelz process. The Waelz process is used for distilling separation of elements under reducing conditions. In this study, a block diagram for production of the following elements from industrial wastes is proposed: zinc, cadmium and indium in form of massive metals; zinc and indium in the form of fine powders; and clinker as a raw material for cement production. The technical and scientific details of this new process have been patented in the Russian Federation and abroad. For the first time, the following operations have been implemented with the use of large-sized Waelz kilns: vapour-oxidized Waelz treatment of polymetallic wastes; recycling of heat from gases and solid products with generation of process fumes; and implementation of alternative flux (dolomite) and alternative fuel (petroleum coke).

Keywords: Waelz process, industrial wastes, heat recycling, vapour-oxidized Waelz processing.

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Over the recent years processing of industrial waste has become of particular relevance. It is obvious that 2017 was declared the year of ecology.

This approach is primarily associated with the fact that Russia is ahead of all economically developed countries in terms of the amount of non-recyclable waste per capita. At the same time, the metallurgical industry produces the majority of wastes.

More than 1 billion tons are accumulated in tailing dumps:

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- non-ferrous metallurgy – 800 million tons;
- ferrous metallurgy - 500 million tons.

The main supplier of waste is processing industry:

- electric melting of steel
- autogenous melting of copper-zinc sulfides and matte converting [1].

UMMC is the only Russian producer of zinc ranged the fourth metal in terms of production and consumption.

The growing needs of the Russian Federation in zinc and a whole range of zinc-related metals, such as lead, indium, tin, cadmium and copper are not met by the current output of the existing enterprises due to shortage of raw material. At the same time, the enterprises of ferrous and non-ferrous metallurgy, chemical industry have accumulated hundreds of millions of tons of zinc-containing waste of 2-4 hazard classes, processing of which will not only contribute to the plant raw material base, but will also improve the environmental situation.

The economic feasibility of extraction of zinc, lead, tin and indium is shown in Figure 1.

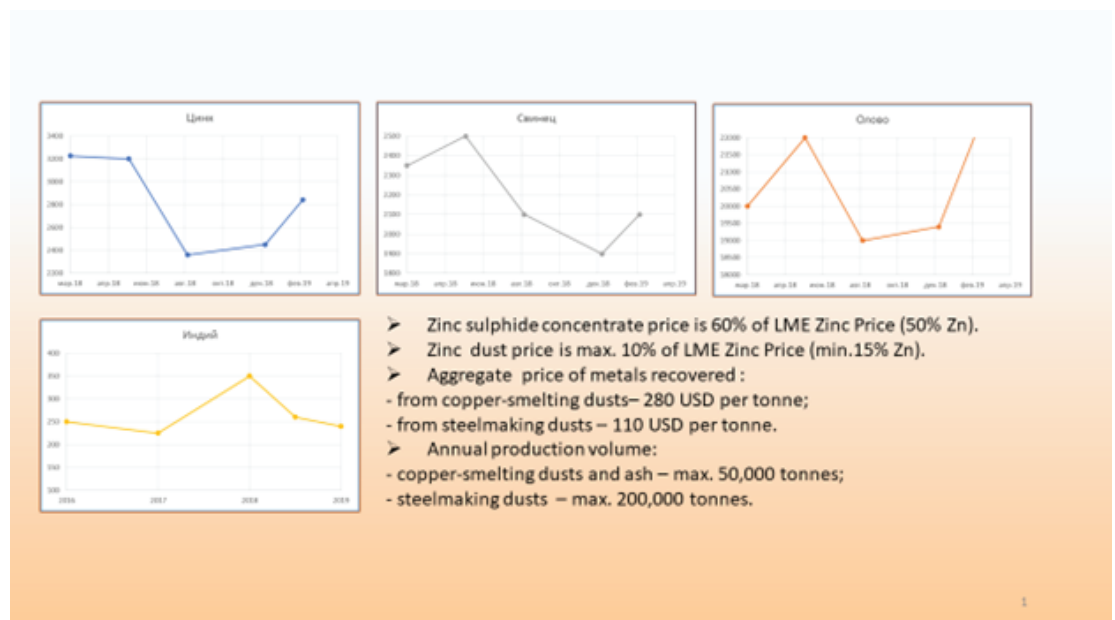


Figure 1: Economic feasibility of dust recycling.

The resulting toxic dust is stored in tailing ponds and dumps. Until now, in Russia these dusts and tailings have not been processed due to their complex chemical and mineralogical compositions, which differ significantly from raw materials as well as the lack of technology to recover all metals from this type of waste.

These wastes as well as previously unprocessed and stored wastes of ferrous and nonferrous metallurgy and chemical industry can be used for primary recovery of the following metals: zinc, lead, tin, indium, cadmium, cobalt, copper, gold and silver.

The presence of the first metal (iron) and the fourth (zinc) in the waste creates a typical problem of their separation.

Many hydrometallurgical and pyro-metallurgical processes have been developed, but it is the Waelz process, which is currently used for processing of more than 85% of the dusts from processing of iron-containing scrap, that has been successful [2–6].

The Waelz technology is based on the separation of the elements of multicomponent oxide systems by distillation under reducing conditions [7].

The Waelz process is intended for processing of oxidized raw material and due to its versatility allows to process chemical industry wastes in addition to ferrous and nonferrous metallurgy wastes.

It can be used to extract zinc, lead, tin, indium, cadmium, mercury, arsenic and antimony (see Figure 2).

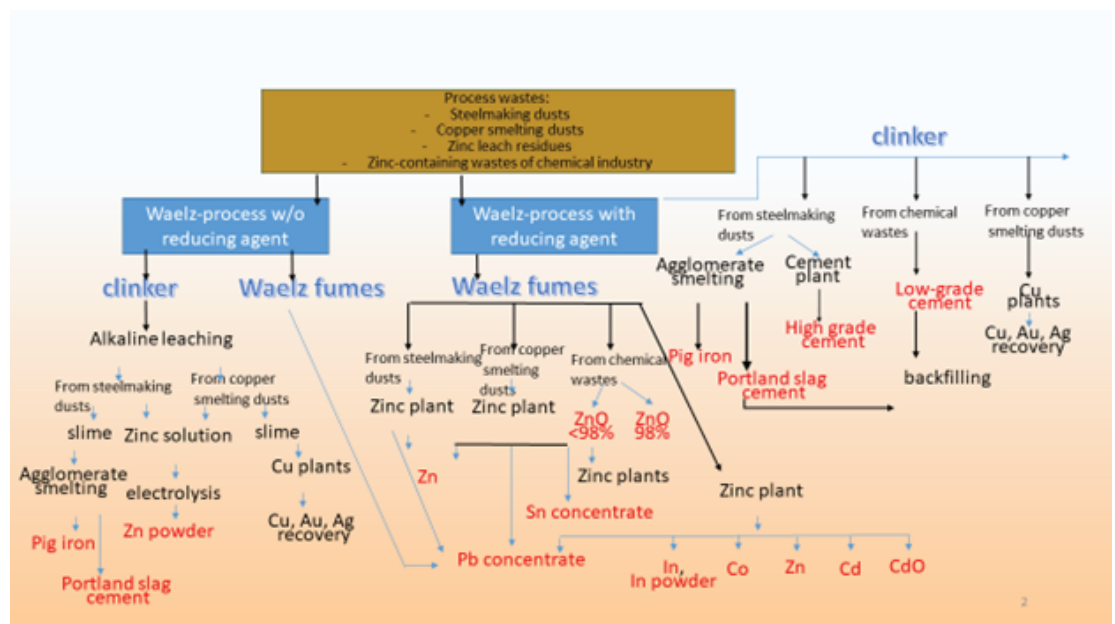


Figure 2: Process waste recycling flow chart.

Some of these metals are distilled in the form of metal vapors (zinc, cadmium), some in the form of sulfides (lead, tin, arsenic), chlorides (indium), oxides (lead, arsenic, antimony).

Alloy of copper and precious metals remains in the clinker feeding the copper processing plants.

Indium and cobalt are extracted by electrowinning technology from leaching solutions of Waelz fumes.

Tin and lead in the form of lead and tin concentrates are processed at lead and tin plants.

Electrolysis is used to produce metallic zinc, cadmium, indium and zinc powder.

Processing of steel electric melting dusts

Table in Figure 3 shows that the selected waste types contain very significant amounts of zinc and related lead, tin, and copper (copper production dust), iron (steel production dust), and indium (zinc leaching residue). However, the increased content of halides in the waste, which prevent the release of zinc at the stage of zinc electrowinning from the solution after leaching, requires technology for their removal.

description	Zn	Pb	Sn	Fe	Cl	F	As	CaO	SiO ₂	Cu	In
Steelmaking dusts	15-20	0.2-5.0	-	11-36	0.4-6.0	0.2-0.4	-	-	-	-	-
Copper smelting dusts	17-25	10-30	2-4	5-10	1.5-2.6	0.1-0.3	0.1-2.5	0.2-4.0	2-8	3.5	-
Zinc leach residues Zinc cakes	18-21	1.5-5	-	13-30	0.05	-	-	0.5-0.8	4-6	-	0.02-0.1
Zinc-containing waste of chemical industry	15-18	0.03-0.4	-	1.5-1.8	0.12	-	-	18-20	8.0	-	-

Figure 3: Chemical composition of zinc-containing process wasted.

Phase analysis of such a complex product as electrometallurgical dust was carried out with integrated use of X-ray and Mössbauer spectrometry complementing each other, as well as electron microscopy.

Zinc in EAF dust is contained in both ferritic and oxide forms. Moreover, there are sodium and potassium chlorides, graphite, magnesite and calcite.

To find out the form of iron in dust, Mössbauer analysis was performed. Two systems of hyperfine structure (HFS) lines with effective magnetic fields H_{ef} of 489 and 459 kOe and a zinc ferrite doublet with isomer shift $\delta E_1 = 0.34$ mm/s and a quadrupole splitting $\Delta EQ = 0.51$ mm/s were found on the Mössbauer spectrum of EAF dust sample. At the same time, 66.2% of iron atoms are part of $ZnFe_2O_4$, and 33.8% of iron atoms are part of Fe_3O_4 , which correlates with quantitative assessment of x-ray phase analysis.

The results of physicochemical studies made it possible to characterize electric furnace slimes as technogenic multicomponent micro-sized oxide powder materials based on iron oxides containing zinc. The concentration of zinc in slime mainly depends on the total amount of zinc in scrap metal used in charge.

Phase analysis of the dust obtained by melting copper was carried out by x-ray phase method.

The calculation of the main reflexes intensities made it possible to distinguish predominant phases of copper smelting dust.

Dusts, unlike ferrous metallurgy dusts, contain much lead and also tin.

X-ray phase analysis indicates the presence of lead in the form of sulfate and sulfide, of lead – in the form of orthostanate, ferrite and sulfide and of copper - in the form of chalcopyrite.

Lead is present in the form of sulfate and sulfide by 85-90%. The remaining amount of lead (about 10%) has silicate or oxide form.

For zinc extraction, zinc concentrates go through two stages: pyrometallurgical (firing in fluid bed furnaces) and hydrometallurgical.

The products of roasting in fluid bed furnaces are treated with solutions containing sulfuric acid in order to transfer zinc to solution. After leaching, the solution pH is 4.7-5.2. As the result of leaching, zinc leach residues- zinc cakes and zinc-containing solutions - are formed.

Zinc cakes consist of residual zinc sulfide (sphalerite), zinc ferrites, newly formed copper sulfide and iron compounds cemented with a finely dispersed flocculent substance of sulfate-hydroxide composition with inclusion of zinc oxide and goethite.

The indium content in zinc cake is 0.02-0.1%.

Besides ferrous and non-ferrous metallurgy waste, more than one million tons of zinc-containing waste of chemical industry have accumulated at landfills.

The presence of zinc in the slime was established as 23.7% of carbonate and 1.5% of hydroxide, calcium - as 26.5% of sulfate dihydrate, 8.7% of carbonate and 14% of free silica, carbon - as 8.2% of organics.

The variety of phase and chemical composition of each waste shows that in order to turn a scientific and technical idea into a specific process, it is necessary to know the behavior of components under Waelz conditions and to develop methods for metals extraction based on the data obtained.

From the data on phase and chemical composition of wastes, we can see significant difference in both quantity and quality of their components. Therefore, it was necessary to find solutions for each type of waste.

The latest development in Waelz process was design and construction of Waelz complex No. 6 with a Waelz kiln 60 m long and 4 m in diameter at PJSC Chelyabinsk Zinc Plant. The Waelz complex No. 5 put into operation in 2007-2008 was taken as a basis. The hardware diagram of Waelz complex is shown in Figure 4.

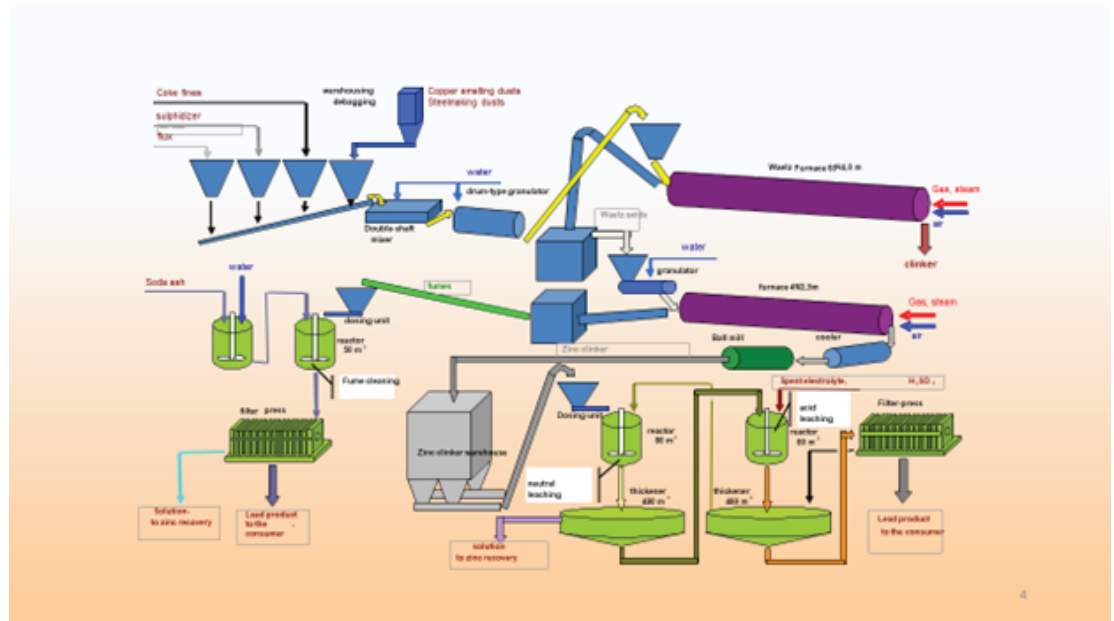


Figure 4: Steelmaking dusts and smelting dusts recycling flow chart.

The designed process flow diagram and engineering solutions, industrial application, differing from the globally known ones used for processing of the crude ore, processed and antropogenic zinc-containing raw materials were developed on the basis of the research and include the following main stages:

- steam oxidative Waelz treatment (1) of raw materials with fuming of zinc, lead, indium and tin in a tube furnace and conversion of copper into clinker transported to copper smelters, as well as iron-containing clinker which is transported to ferrous metallurgy productions [8, 9];
- preparation of raw materials for metallurgical processing, eliminating the loss of materials and ensuring the effectiveness of subsequent pyrometallurgical processing [10];
- pyro-selective Waelz treatment (P) of the oxide from Waelz treatment (1) with release of lead fumes, their further condensation, washing and obtaining concentrate, as well as zinc-containing clinker [11];
- leaching of zinc-containing clinker to obtain zinc-containing solution and lead or lead and tin cake which is transported to the productions of these metals;
- extraction of indium from the solution (in the processing of zinc cakes)
- electrolysis of a zinc-containing purified solution to obtain commercial zinc.

- electrolytic refining of indium to produce commercial indium.

Original world class solutions are:

- process of steam oxidative Waelz treatment of polymetallic wastes, providing 99% recovery of zinc, 98% of lead and 93% tin, which is 4% higher than the known analogues;
- recycling of heat from gases and solid products, with the production of process steam, providing at the same time two-fold reduction in energy costs in comparison with the best foreign counterparts;
- designs of Waelz furnaces, a waste heat boiler and filters, ensuring a reduction in dust content of exhaust gases to 0.4-0.7 mg/m³ (European standard - 5 mg/m³);
- the versatility of technology that enables processing of dust from non-ferrous and ferrous metallurgy, waste from galvanic shops, spent catalysts, waste, etc. [11, 12];
- conversion of harmful elements (As³⁺, Cl⁻, F⁻) into low-toxic compounds with their subsequent use in industry (ferrous metallurgy) and construction (roads, etc.) [13, 14];
- recovery from wastes of zinc and additional metals: indium, tin, lead, cadmium;
- methods for improving the quality of marketable products and the sequence of operations providing selective separation of multicomponent waste elements;
- obtaining a wide range of powders: indium powder - by disproportionation method (Figure 5), zinc powder by electrolysis (Figure 6), cadmium oxide from a cadmium sponge (Figure 7) [15].

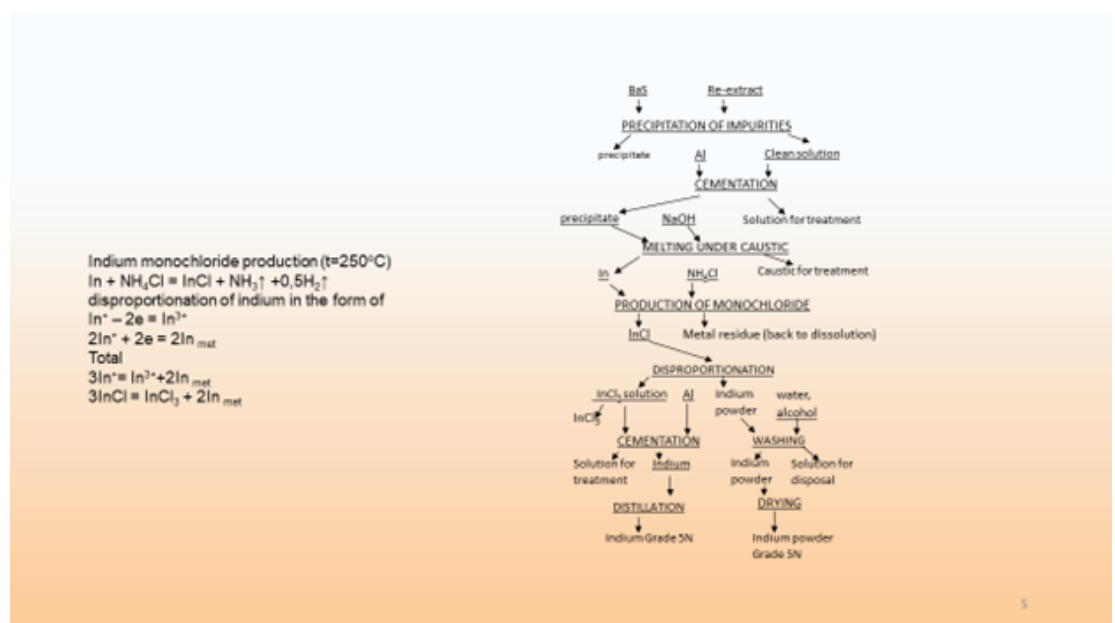


Figure 5: High-grade indium powder production chart.

There are no equal technologies for joint processing of dusts from non-ferrous and ferrous metallurgy in world practice. Engineering solutions and know-how can be

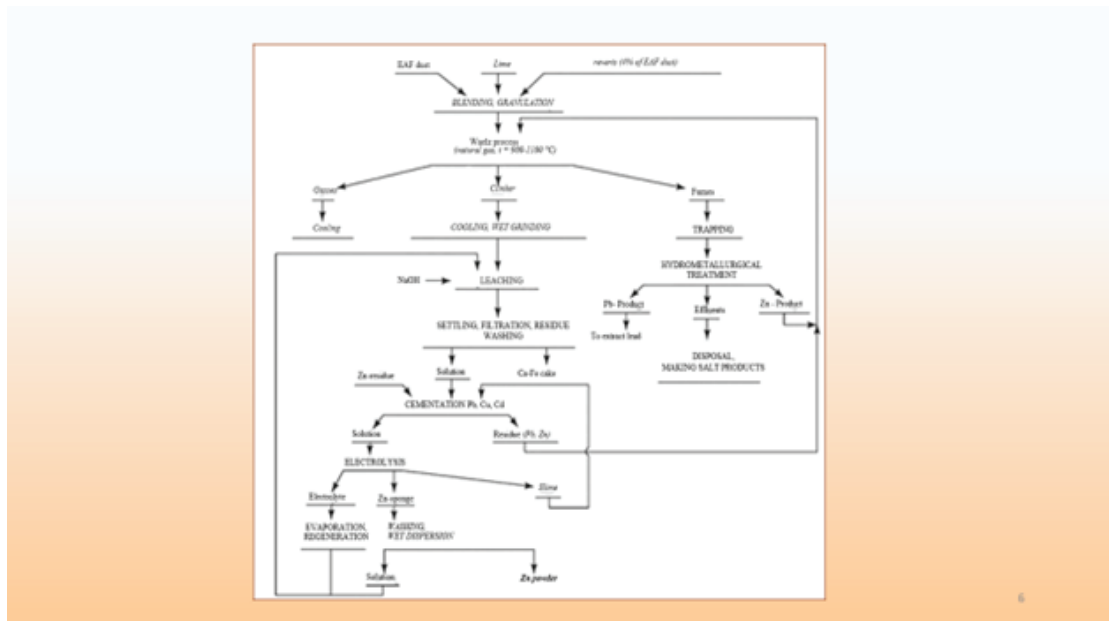


Figure 6: Ferrous zinc dust recycling flow chart.

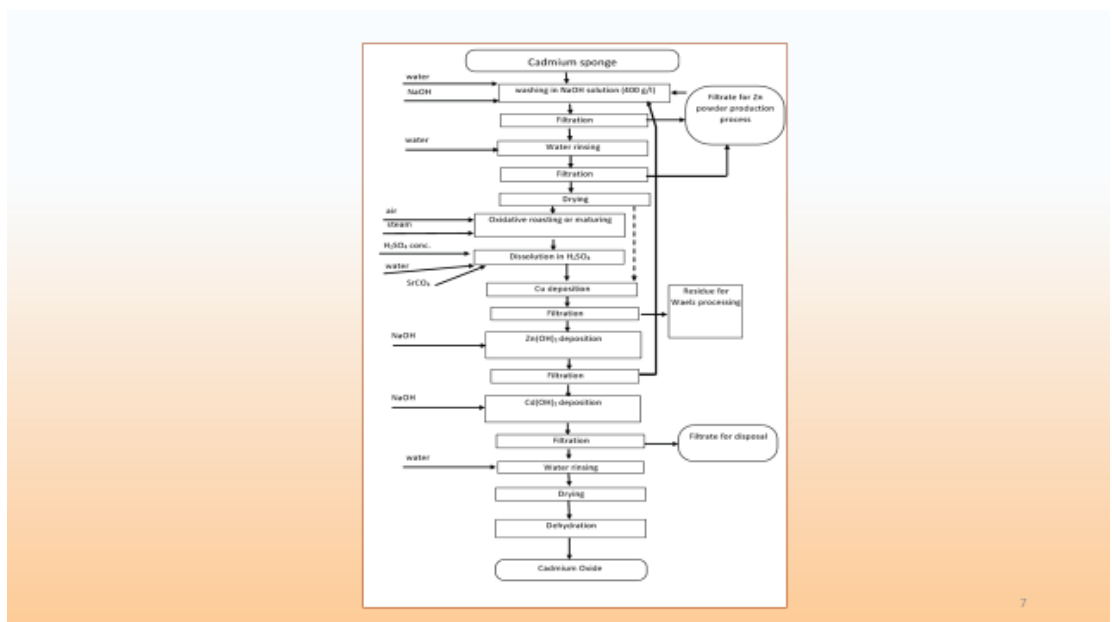


Figure 7: Cadmium oxide powder production from cadmium sponge.

exported abroad (Germany, USA, Bulgaria, Brazil, etc.). A number of patents are currently being patented in Germany.

The development of a physical and chemical basis and engineering solutions for the extraction of the gamut of non-ferrous (zinc, lead, copper, tin, cobalt), rare (indium and cadmium) metals, as well as iron in the form of metals or powders, salts and oxides from industrial and chemical waste improves ecological situation in areas where industrial enterprises are located.

Since 2010, all the dusts of copper smelters of UMMC (more than 30 thousand tons/year), and waste products from ferrous metallurgy enterprises (more than 13 thousand tons/year) are processed annually.

The new technology is being widely used: a large-sized Waelz kiln 60x4m is under commissioning at PJSC “Chelyabinsk zinc plant”, and in Nizhny Tagil a furnace 60x3 m is being commissioned according to the process procedure developed by the UMMC Technical.

The Waelz complexes are being designed according to the regulations of TU UMMC in Abinsk, Nevinnomyssk, Balakovo. This will make it possible to process almost all of the zinc-containing dusts generated annually in the country from copper smelting and electric steel production and to proceed with the processing of previously buried waste.

Within the framework of the work, two important economic problems are solved: providing the metallurgical industry with high-quality raw materials and solving the environmental problem associated with the disposal of waste of hazard classes 2-4, with a reduction in the content of dust emissions in Waelz process from 10 mg / nm³ under the project to 0.4- 0.7 mg / nm³ (the European standard requires 5 mg / nm³), a decrease in annual CO₂ emissions of 2 million m³.

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