IMPROVING TECHNOLOGY AND SETTING-UP A PRODUCTION LINE FOR HIGH QUALITY ZINC OXIDE (99.5%) WITH A CAPACITY OF 150 TON/YEAR BY REDUCTION-OXIDATION PROCESS

Pham Minh Tuan, Tran The Dinh, Tran Ngoc Vuong, Tuong Duy Nhan, Tran Trung Son, Le Huu Thiep, Nguyen Trung Dung, Le Thi Hong, Luong Manh Hung and Bui Huy Cuong

Center for Technology Development,
Institute for Technology of Radioactive and Rare Elements, Vietnam Atomic Energy Institute
48- Lang Ha, Dong Da, Ha Noi

Project Information:

- **Code: HĐDA. 06/2010/NLNT**
- **Managerial Level: Ministry**
- **Allocated Fund: 1,700,000,000 VND**
- **Implementation Time: 42 months (Mar 2010-Aug 2013)**
- **Contact Email: pmtuan1258@yahoo.com**
- **Papers published in relation to the project: (None)**

ABSTRACT: Zinc oxide is used not only for the rubber industry, but also in many other industries such as pigments, ceramics, cosmetics etc. On the basis of references on international scientific researches and practical activities for the production of zinc oxide in our country, we have carried out additional research and testing to establish a zinc oxide production line for preparation of high quality (99.5%) product by treating the industrial zinc containing waste to obtain required composition materials [Zn] >50%; [Pb] < 0.3%; [Cl]/[PbO] < 0.2 for reduction-oxidation processes using reverberatory furnace.

Keywords: *Zinc oxide; reduction oxidation method; american process; direct zinc oxide.*

1. OVERVIEW

Reduction-oxidation method (American process) is the most important method for the highest capacity production of zinc oxide at present. Most industries are using ZnO produced by this method.

The resulting product by this method is often not of high quality, depending on the type of raw materials, which can be obtained with a concentration of ZnO 70% to 99%. Along with the advancement of science and technology today, ZnO produced by this method can reach the higher quality zinc oxide of 99.5%.

Basically, the method consists of following stages: 1)materials processing; 2)reduction of zinc oxide in the materials into metallic zinc by using coal, coke; 3) then zinc metal at high temperature will be evaporated and react with oxygen in the air to form zinc oxide.

Reduction oxidation method is carried out by means of two basic types of devices: the rotary kiln and reverberatory furnace.

The reverberatory furnace method is currently most commonly used to produce ZnO thanks to its high quality products. This method has the advantage of a favorable investment due to low cost, simple device, easily to fabricate. The downside of this method is its rather low recovery performance compared to the method using a rotary kiln: typical recovery efficiency of zinc is around 90%.

Technology fundamentals

The chemistry of the production process by reduction-oxidation method can be represented by the following reaction equation:

$$ZnO\ (solid) + CO = Zn\ vapor + CO_2 \qquad (1)$$

$$Zn\ vapor + O2 = ZnO\ (solid) \qquad (2)$$

During the reduction-oxidation of zinc, lead (Pb) content in the raw material will have a similar behavior to zinc. Pb content in ZnO product by this method highly depends on the Pb content in raw materials. In addition, quality of the resulting ZnO product obtained by reduction-oxidation process depends mainly on two other factors: temperature of reverberatory furnace and chloride salt content in raw materials.

2. TECHNOLOGY IMPROVEMENT

We have implemented this project with the following specific measures:

1. Research a method of Lead separation, while minimizing Pb and chloride salt concentrations in raw materials.

2. Change reverberatory furnace design to increase impurity removals efficiency and improve the furnace performance.

3. Use material pressed pellets instead of powder materials, and design, set-up a dust handling systems for reduction-oxidation furnace to improve efficiency of reduction-oxidatition process.

2.1. Lead removal

The reaction of Pb separation process is represented by the following reaction equation :

$$2NaCl + PbO + 2SiO_2 + Al_2O_3 = PbCl_2\uparrow + 2NaAlSiO_4 \qquad (1)$$

$$2NaCl + PbO + CO_2 = PbCl_2\uparrow + Na_2CO_3 \qquad (2)$$

$$2NaCl + ZnO + CO_2 = ZnCl_2\uparrow + Na_2CO_3 \qquad (3)$$

According to [19] , the reaction (1) occurs at temperatures of 900-1000^{0}C, the reaction time of about 90 minutes, the activation energy for reaction (1) is 175 kJ/mol, the reactions (2) and (3) can occur at lower temperatures (800-1000^{0}C).

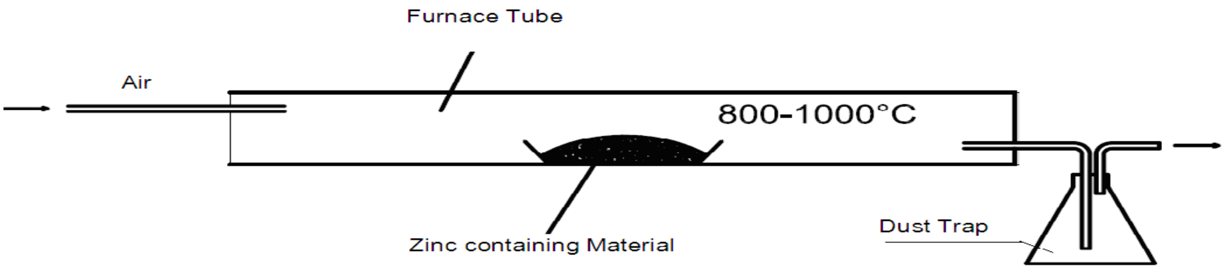

Figure 1: Schema of Lead removal experiment.

The experiment results have been shown in the table 1.

Table 1: Pb removal study by chlorination method.

Sample	Con.,%	Reaction temp.,^{o}C	Reaction time, min.							
			15	30	45	60	75	90	105	120
M1	Zn 67.5 Pb 2.70	850	2.65	2.5	2.2	1.7	1.3	1.1	0.7	0.55
		900	2.6	2.4	2.05	1.5	1.1	0.9	0.65	0.55

	Cl 6.1	950	2.6	2.2	1.85	1.2	0.85	0.7	0.55	0.4
		1000	2.55	2.15	1.75	1.05	0.7	0.55	0.5	0.4
M2	Pb 3.6 Cl 6.2 Zn 67.0	850	3.55	3.3	2.7	2.35	1.55	1.05	0.9	0.85
		900	3.55	3.25	2.55	2.2	1.55	1	0.8	0.8
		950	3.5	3.2	2.5	2.0	1.4	0.9	0.8	0.7
		1000	3.5	3.1	2.4	1.9	0.95	0.85	0.75	0.7
M3	Pb 3.6 Cl 6.2 Zn 67.0 3%NaCl	850	3.55	3.3	2.7	2.35	1.55	0.8	0.55	0.5
		900	3.55	3.25	2.55	2.2	1.55	0.8	0.55	0.5
		950	3.5	3.2	2.5	2	1.4	0.7	0.5	0.45
		1000	3.5	3.1	2.4	1.9	0.95	0.7	0.45	0.45

When the concentration of Pb in raw material is lower (experiment 1), Pb removal process showed its good efficiency. In the case of high Pb concentrations, although the reaction time extended to 120 minutes, even at temperatures of 1050^{0}C (the highest temperature in the temperature range survey), amount of Pb remained in the reaction mass was still higher than the value required (experiment 2).

This phenomenon can be explained that, chlorides containing in the reaction mass was disintegrated so chloride amount remained could not be enough to transform all Pb containing in the raw material to lead chloride, therefore chloride salt should be added to the reaction mass to suply additional chloride for the chlorination reaction (experiment 3, fig.2).

From the experimental results, we could see that, when chloride is added in the form of sodium chloride, Pb separation efficiency increases even though the amount of chlorine in the starting material is very large compared with the Pb content in the material.

The additional amount of sodium chloride is calculated according to [19,25]. The verification experiment showed that NaCl salt should be added so that the total amount of chloride in the reaction mass was about 3 times larger (in stoichiometric) compared with Pb content in raw materials.

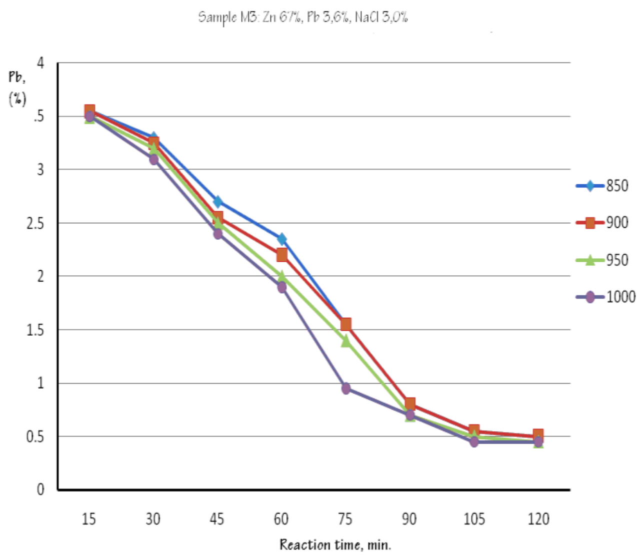

Figure 2: Lead removal test (Sample tested No.3).

Through empirical data survey of Pb separation process, following conclusions can be made:

1) Pb removal process will achieve good efficiency at temperatures in the range 800-1000^{0}C, the time needed to maintain the reaction temperature is 90 minutes.

2) Pb contain in the zinc slag can be reduced to the value of 0.4%.

3) When the concentration of Pb in the zinc slag is high, chloride in the form of sodium chloride should be added to provide reacting agent for chlorination reaction.

4) This method can simultaneously solve both the most important issues: removal of Pb and reduction of chloride contained in the raw material.

2.2. Reduction-oxidation furnace set-up

We have changed the design, creating two separate zones in the furnace: Reduction Zone and oxidation Zone. Air supply for oxidation process is fed into the oxidation chamber through the intake air (see Fig.3).

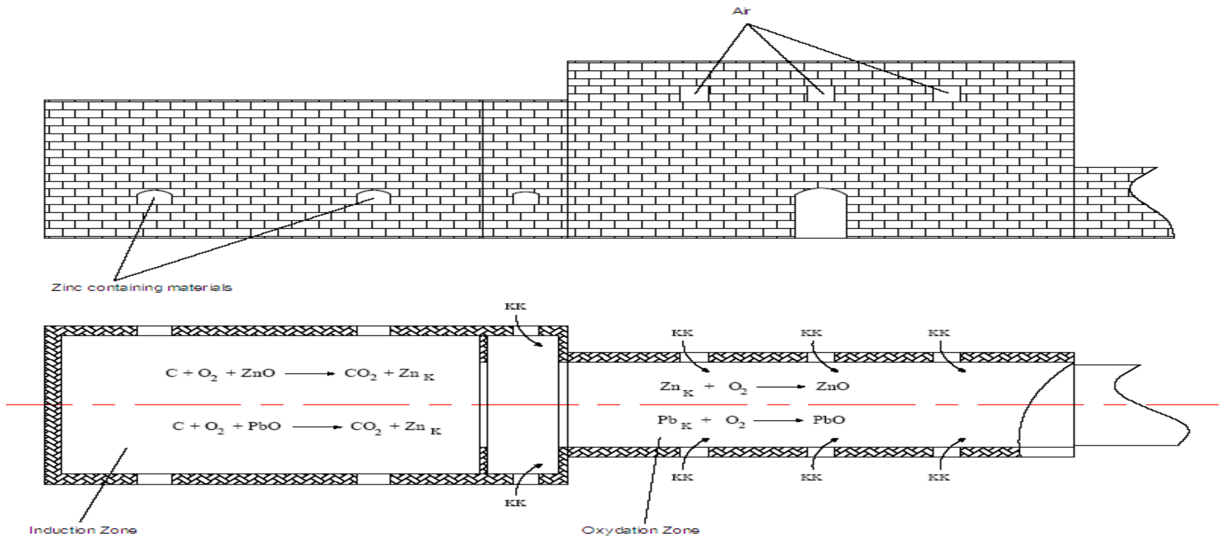

Figure 3: Reverberatory Furnace Design Improvement.

Based on additional research, a system of devices are listed below.

1	Reverberatory furnace for Reduction-Oxidation of Zinc: Productivity 600kg/batch; 02 blower power 4 kW; 18000 -20000m^3 /h, pressure 250 mmH_2O; Drain system of 10 chambers deposition system made of SUS304 stainless steel.
2	Dust collection system with bag house, filter surface area: 300m^2; dust collection fan of 350mmH_2O pressure, flow 12.000m3/h. Working temperature: <100°
3	Ball press machine, Model YBM430: Rolls diameter 430 mm.Capacity: 6-8 t/h. Motor power: 11 kW.
4	Grinding machine Model ZC-800: Grinding Barrel Diameter: 800 mm.Capacity of 10 ton/h. Motor 30 kW.
5	Mixing Machine, Model YZM-300: Length 3000 mm; Mixing tank 2500x550mm; Mixing velocity: 40 v/ph.

3. TRIAL PRODUCTION

Five trials with different composition materials have been done. Each test is carried out by using 20 tons of zinc slag processed. It has been confirmed:

- The measures applied to improve the quality of materials is a suitable solution to produce zinc oxide of desired quality.
- The reduction-oxidation furnace system has ability to produce high quality zinc oxide with the appropriate material.
- Standard input for the production of high quality zinc oxide by reduction-oxidation method : [Zn]> 50%; [Pb] <0.3%; [Cl] / [PbO] <0.2.

Table 3 below discribes the composition of pretreated material (to reduce Pb and Chloride).

Table 3: Pretreated material composition.

	Zn	**Pb**	**Cl**	**Mass remained,%**
X1	76.0	0.36	0.23	100
X2	75.4	0.48	0.22	94

Table 4: Raw (untreated) material composition.

No.	Species		**M1**	**M2**
1	ZnO	%	76,9	75,4
2	Pb		0.73	0.41
3	Clo	%	1,7	2,1
4	Mn	mg/kg	192.16	348.02
5	Fe		6330.4	6066
6	Mg		34.92	51.12
7	Ca		34.14	24.12
8	Na		87.33	164.59
9	K		65.48	92.77
10	Si		156.06	256.18

Procedure for high quality inc oxide production.

The production procedure and technical parametters required for each stage have been shown in the fig.5 below.

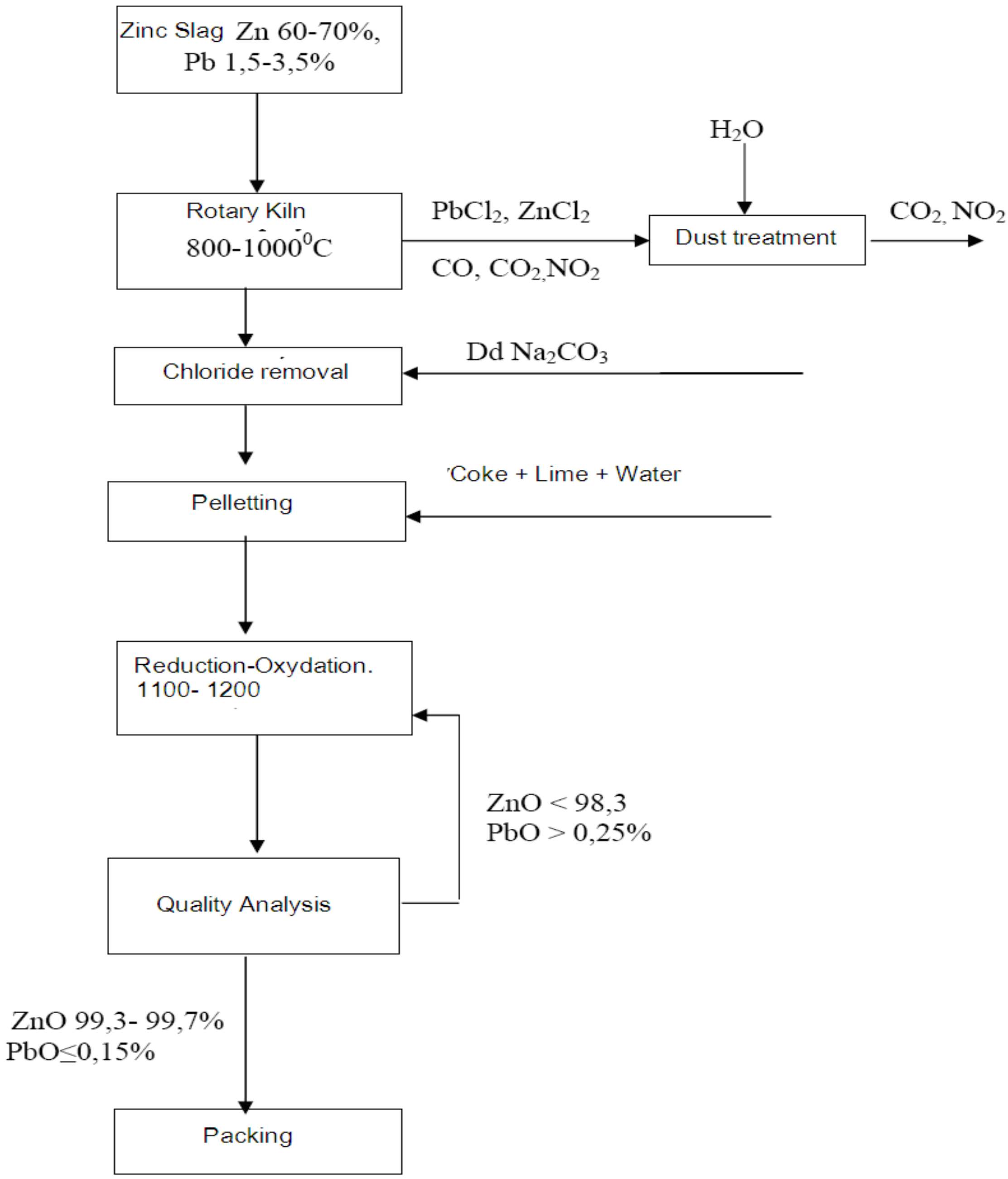

Figure 5: Technology schema for high quality zinc oxide(99.5%) production line.

Table 5: Analysis and assessment of product quality.

No.	Species	Analysis method	Results	Examiner
1	ZnO	ISO13658(E)	99.52%	*Analytical Center, Lab Vilas 143- Istitute for Mining and Metallurgy.*
2	Pb	ISO5889(E)	0.15%	
3	Fe	ISO5889(E)	0.003%	
4	Particles Size	LSPSDistribution Analyser LA-950	5-10μm	*ITRRE.*

4. CONCLUSIONS

- The Project "Improving technology and setting up a production line for high quality zinc oxide (99.5%) with a capacity of 150 ton/year by reduction-oxidation method" has been implemented as registered in the Project Notes. Specifically:

- *Technology improvement*: The Projects completed all technology items, aimed at the stages of production of zinc oxide, especially focused on the process of the raw material heat treatment in a rotary kiln. By using pretreated zinc containing materials, ZnO product meet all requirements of rubber grade high quality zinc oxide even quality of zinc slag material is not high. The main technological parameters have been established and a new zinc oxide production line by reduction-oxidation process has been built.

- *Technology equipment:* A new Production line equipment mainly focused on the enhancing process efficiency and increasing product quality. The material pelleting technology is a key solution in production technology. Dust collection system, gas treatment combined with material pelleting technology have brought about economic efficiency: increasing product revenue performance and meeting environmental protection requirements.

- *Production:* The total amount of product produced during the time of implementing the project was 455 tons. Zinc oxide products met all the requirements of vulcanized rubber technology. In fact, the production cost will be reduced at a larger production scale by the depreciation of equipment and less labor consumption.

REFERENCES

[1] PHẠM QUANG TRUNG, ***Nghiên cứu quy trình nung phân huỷ*** $ZnCO_3$ ***thành ZnO trên thiết bị nung động***, Báo cáo tổng kết đề tài CS-99-13, Viện Công nghệ Xạ-Hiếm, Viện Năng lượng Nguyên tử Việt Nam, Hà Nội 4/2000.

[2] YUREN JIANG, ET AL, ***Preparation of High Purity Zinc Oxide from Zinc Metal Scrap***, Akita University and the University of Tokyo-Japan.

[3] G. HEIDEMAN, ***Reduced zinc oxide levels in sulphur vulcanization of rubber compounds.*** Ph.D. Thesis, University of Twente, Enschede, the Netherlands, 2004.

[4] BERGENDORFF O., PERSSON C., HANSSON C., ***Chemical changes in rubber allergens during vulcanization.***
Department of Dermatology, University Hospital, Lund University, Sweden.

[5] DANIEL L. HERTZ, JR., ***Theory & Practice Of Vulcanization***, Seals Eastern Inc., Red Bank, NJ 07701.

[6] LUTAO LI, ET AL, ***Formation of ZnO-containing Dust from Zn-bearing Steel Melts***, Technical University of Claustahl-Germany, July 25, 1994.

[7] HIROYUKI MATSUURA, ET AL, ***Removal of Zn and Pb from*** Fe_2O_3-$ZnFe_2O_4$***-ZnO- PbO Mixture by Selective Chlorination and Evaporation Reactions***, The University of Tokyo-Japan, January 30, 2006

[8] www.omnexus.com, ***Review of vulcanization chemistry***.

[9] J.G.KREINER, ***Method for improving rubber curing rates***, US Pat. 4882394, 11/1989.

[10] CHSSR KUMAR, AVINASH M NIJASURE, ***Vulcanization of rubber***, ICI Research and Technology Center, Thane, India..

[11] ***Treatment of polyvinylchloride***, US patent 5698759.

[12] ***Treating Lead and Zinc-containing steelmaking by-products***, US patent 4765829.

[13] ***Chloride melt process for the separation and recovery of Zinc***, US patent 6931474.

[14] JAE-MIN YOO, BYUNG-SOO KIM, MIN-SEUK KIM AND JINKI JEONG, ***Separation of Lead and chlorine from electric arc furnace dust to recover Zinc,*** Korea Institute of

Geoscience and Mineral Resouces, 3/2007.

[15] JOHN HENRY CALBECK. ***Production of Zinc oxide***, US patent 2 603 554.

[16] BECKMANN ET AL. ***Treating Lead and Zinc containing stellmaking byproducts***, US patent 4 765 829.

[17] SHUGARMAN, ***Lead removal method***, US patent 4 704 260, 11/1987.

[18] FRANK G. BREYER, EARL C. GASKILL ET AL. ***Manufacture of Zinc Oxide***, US patent 1522097.

[19] M.P. KIRK. ***Apparatus for Producing Zinc oxide***, US patent 1566103.

[20] *DA02/2005*. ***Hoàn thiện công nghệ sản xuất kẽm cacbonat.*** Viện Công nghệ Xạ-Hiếm, Viện Năng lượng Nguyên tử Việtnam, 6/2007.

[21] A.M.LASTOTSEV, E.I. GORODNICHEVA, ***Calcualting power consumption for mixing high-viscosity newtonian liquids with blade mixers***, UDC 66.063.

[22] DAT-NLNT/06-04, ***Hoàn thiện công nghệ và dây chuyền thiết bị cho sản xuất ZnO 98,5% quy mô 150tấn/năm***, Hà nội 12/2008.