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Development of an Energy-Saving Melting Reactor for Energy-Efficient Disposal of Slag Dumps

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Abstract: Millions of tons of slag and clinker can be found in the dumps of enterprises across the Republic of Kazakhstan. The goal of this project is to create a technology that conserves energy in waste treatment. The novelty of the work is the discovery of a new phenomenon, which shows that in the melt layer, there are two reactions opposite in direction and intensity: slow reactions of the decomposition of complex components into simple molecules and rapid responses of the formation of complex components from simple molecules. The dominance of one of the two reactions affects the process's fuel consumption. Using this phenomenon, a melting reactor was created, which will reduce specific fuel consumption by 3–4 times compared to a Waelz kiln. It is shown that using a new method of CO_2 decarbonization by zinc, it is possible to ensure the production of zinc sublimates and cast stone products and the full neutralization of CO_2. The lowest market potential only for Achisai dump clinker would be around USD 125,600,000 if the cost of commercial clinker sublimates is USD 800/t. The expected net profit would be USD 4,466,039/y.

Keywords: slag; clinker; zinc; "ideal" mixing–displacement; casting stone

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1. Introduction

The insufficient complexity of mineral processing in the Republic of Kazakhstan leads to losses of 20–30% of the recorded raw material reserves. Over 17 billion tons of solid waste have accumulated in the dumps of enterprises, in which the content of valuable components is often higher than in ores [1,2]. The shift to a circular economy is a viable strategy for attaining sustainable mining industry development at this point. Finding the best way to use mining tailings in accordance with circular waste management is the scientific aim [3]. Industrial waste produces the largest amount of toxic formations. Therefore, the most important scientific and practical task is to improve the processing of raw materials to create energy-saving, waste-free technology and eliminate harmful emissions into the atmosphere and soil.

Several such processes are currently used industrially in the world, Kaldo (Sweden), Queneau–Schuhmann–Lurgi (QSL, Germany), Top Submerged Lance (TSL Australia), oxygen-suspended electrothermal smelting (KIVCET, Kazakhstan), Shui Koushan Smelting, (SKS, China) [4–6], and others, which are used to process rich ore. "Rich" slags from factory storage facilities, with a zinc concentration of up to 10–12%, are processed using the Waelz method. The essence of the process is that the zinc-containing dispersed material is mixed with coke, and at the maximum temperature that excludes melting of the material, the batch is stirred for uniform gasification of the coke and distillation of zinc throughout the entire mass of the batch. The coke contained in the charge serves as fuel, reducing agent, and "drying agent"—a substance that absorbs the molten part of the charge. Therefore, the amount of coke in the charge is greater than necessary for combustion, and the "drying" part of the coke remains in the clinker.

The main objective of the process is to separate zinc from most of its associated components in oxidized industrial and ore zinc-containing materials. This goal is achieved because, under conditions of carbothermic reduction, zinc passes into a metallic state, in which its volatility is much higher than the volatility of other components accompanying it under the same conditions. The Waelz process can be used to extract zinc, lead, cadmium, arsenic, antimony, bismuth, and tin from a wide variety of materials.

The main characteristics of the operating Waelz kilns are as follows: length/diameter ratio, 30/2.2, 41/2.6, 50/3.6, an d90/4.5; tilt angle, 2–4% of the length; rotation speed, 0.4–2 rpm; engine power, 40–100 kW; lining material, chamotte and chrome-magnesite; size of the processed material, no more than 10 mm; consumption of reducing agent, 45–55%; gaseous or liquid fuel for heating, 1–10% of the charge mass; and specific volumetric productivity for charge, ~1 t/m^3 per day. The lower limit of the content of distilled metals in the Waelz feedstock is limited for economic reasons, and for zinc, it is usually not lower than 6%. The solid waste of the process is Waelz clinker, which is stored in the enterprise's waste dumps [7].

Of the many methods, the hydrometallurgical method for processing slags is not used in practice due to the toxicity and high concentration of SiO_2 (22–38%). For example, when processing slags with concentrated sulfuric acid, a gel is formed that prevents the release of zinc.

The fluidized bed method for zinc sublimation is also not used due to the relatively low process temperature (700–900 °C).

"Rich" slags with a zinc concentration of up to 10–12% can be processed by electrothermal reduction using nitrogen, by vacuum method, by fuming, or by Waelz. The result is "poor" slags and Waelz clinker with a zinc concentration of 2–4% [8].

However, the lower limit of the economically efficient processing of "poor" slags is 6%. Therefore, the processing of "poor" slags and clinker by traditional methods does not promise benefits. In the work [9,10], it is shown that the processing of "poor" slags requires 2–3 times higher specific energy consumption compared to the processing of "rich" slags. However, there are no technologies in the world for the cost-effective processing of "poor" slags. At best, these slags are used as a corrective additive to cement clinker or in asphalt concrete production. The object of this work is to reduce the energy consumption of processing "poor" slags and clinker by 3–4 times, and to increase the profitability of the process. For this purpose, the authors developed a new method of "ideal mixing–displacing" the melt and created, on its basis, a unit "smelting reactor-rotary kiln" with a capacity of 1.5 t/h for slag. The results of the experiments showed a reduction in energy costs by 3–4 times compared to the Waelz process.

Only in the metallurgical workshop of the Achpolimetall plant have about 4.5 million tons of Waelz clinker accumulated. With the depletion of rich oxide ore reserves, the zinc content in the Achisai mine has decreased to 10–12%. After fluxing the ore, the zinc concentration in the charge did not increase above 6–7%. The low zinc content and the high coke cost led to a complete shutdown of the workshop.

The mass fraction of clinker components, in %, is Cu (0.85–1.20), Zn (1.37–5.00), Pb (0.11–0.38), $Fe_{(com)}$ (13.88–30.30), SiO_2 (29.06–38.11), CaO (9.03–19.03), Al_2O_3 (7.13–11.64), MgO (1.52–2.56), MnO (1.11–1.27), Na_2O (0.03–1.13), S_{com} (2.37–2.55), Au(g/t) (1.8–3.7), Ag(g/t) (65.0–117.0), and C (4.2–15).

Considering that the predicted depletion period for polymetallic raw materials, rich in valuable components, in the Republic of Kazakhstan is 30–35 years, then, soon, the production of metals from technogenic waste and low-ranked ores may turn out to be a priority.

A literature review for the processing methods of clinker from zinc production has shown that a hydrometallurgical method of clinker disposal is considered harmful and corrosive, and gives no comprehensive technological solution for its complete and energy-saving processing [11].

The article [12] provides a comparative analysis of the energy efficiency of hydrometallurgical and pyrometallurgical methods for various materials. From the analyses of these papers, the authors are inclined to believe that the pyrometallurgical method would be suitable for processing clinker.

This work focuses on finding a new method, creating, on its basis, an energy-efficient melting unit, developing environmentally friendly technology for integrated clinker treatment, and forecasting the project's profitability.

The niche for using the unit being developed can be the following dumps of an enterprise in the Republic of Kazakhstan, which have not yet been disposed of: thermal power plants (Zn and Ge contained ash), Leninogorsk polymetallic plant (Waelz clinker), JSC Kazzinc (dump-zinc slag), Achpolimetal plant (Waelz clinker), Yuzhpolymetal plant (dump-zinc slag), Balkhash zinc and Dzhezkazgan copper smelters (copper smelting slag), Karaganda metallurgical plant (zinc-containing dust and blast furnace slag), Syrymbet LLP (tin concentrates), Shalkiya LLP (lead concentrates), and Novo Dzhambul Phosphoric Plant (waste phosphate rock fines).

In non-ferrous metallurgy enterprises, sublimates of zinc, germanium, and gallium (ZnO, Ga_2O_3, GeO_2) are processed into metal zinc, germanium, gallium, arsenide, or gallium nitride or their other compounds, the demand for which is growing in the world.

The main consumer of carbonaceous iron is the Karaganda Metallurgical Plant. Potential consumers of stone-cast paving and curb slabs are construction enterprises of the Republic of Kazakhstan.

2. Method of the Research

The main methodological basis for this work is the physicochemical method for calculating a melting reactor's parameters and the creation, on its basis, of a pilot plant for integrated waste processing, conducting experiments, and the development of a waste-free, energy-saving, and environmentally friendly system for processing slag and clinker.

Based on the physicochemical method and method of affine modeling, and an analysis of the technical and economic characteristics of both traditional methods—a bubbling layer of smelt, and the advanced method, a boiling layer of smelt [13–20]—a new technological method called the ideal mixing smelt layer has been developed [21,22]. In this regard, a pilot plant of the new generation called "melting reactor–rotary kiln" has been constructed, and a series of experiments have been conducted to validate the efficiency of the proposed method. Based on the results of experiments on the pilot plant, the industrial sample has been recalculated, and an environmentally friendly slag-processing thermal diagram is proposed.

The Novelty of the Work Is

- The discovery of a new phenomenon, showing that in the melt layer, there are two reactions opposite in direction and intensity, (1)—slow reactions of the decomposition of complex components (Zn_2SiO_4 and $ZnFe_2O_4$) into simple molecules (ZnO, SiO_2, and Fe_2O_3) and (2)—rapid reactions of the formation of complex components from simple molecules; the dominance of one of the two reactions affects the process's fuel consumption;
- The creation of a new physicochemical method for calculating the technological parameters of a melting reactor;
- A novel approach, a combination of "ideal" mixing and "ideal" displacement patterns, enhancing the level of zinc recovery from 30% to 70%;
- A combination of a melting reactor and a rotary kiln, reducing specific fuel consumption by 3–4 times compared to existing analogs;
- A new mode of iron recovery from clinker, with a residual amount of 9–10%, allowing the simultaneous acquisition of two products, carbon iron and stone castings.

3. Development of a Physicochemical Method for Calculating a Melting Reactor's Parameters

The weight of the bath is the crucial element that affects both the construction and performance requirements of the melting reactor. The following assumptions are used as the basis for its calculation method:

- The molten bath operates in a mode close to ideal mixing. According to this assumption, the zinc concentration throughout the layer is the same and equal to the concentration at the outlet $C = C_f$;
- The melt in the layer consists of particles of equivalent diameter, d_e. The initial concentration of particles entering the layer is C_{in};
- The particles of the layer exist over time τ*, after which they immediately collide, interflow, mix, and re-separate, which leads to the equalization of the concentration in the volume of the particle, and the renewal of the interfacial reaction surface;
- For the entire set of particles, the lifetime τ* is the same;
- Over time τ*, the melt particles are dezincified according to the law of non-stationary internal diffusion under boundary conditions of the first kind (particle surface concentration C_{sur} = 0, since the limiting stage is the internal mass transfer). In this case, the amount of zinc removed from the particle during time τ* is determined from the following expression [23]:

$$\Delta g(\tau^*) = \frac{\pi d_e^3}{6}\rho_m\left[C_f - C(\tau^*)\right] = \frac{\pi d_e^3}{6}\rho_m C_f(1-\theta) \quad (1)$$

Here, ρ_m is the melt density and $C(\tau^*)$—particle average volume zinc concentration as a function of time.

$$C(\tau^*) = C_f\left(1 - \frac{6}{\sqrt{\pi}}\sqrt{Fo_d} + 3Fo_d\right), \frac{C(\tau)}{C_f} = \theta, \quad (2)$$

where $Fo_d = D_{ZnO}\cdot\tau^*/r_e^2$—Fourier diffusion criterion (dimensionless time), and θ—particle's medium volumetric dimensionless concentration of ZnO. The number of particle collisions in the "ideal mixing" layer [24], leading to complete dezincification is $n = 1.443ln\frac{C_{in}-C_f\theta}{C_f(1-\theta)}$.

Then, $\tau* = \frac{\tau_{mix}}{n}$, where τ_{mix}—time of melt complete mixing in the layer. τ_{mix}—is determined by the criteria equation obtained based on an experimental study of the gas–liquid model of the melting reactor [24].

The required particle amount in the bath is

$$N = \frac{P\left(C_{in} - C_f\right) \cdot \tau^*}{\Delta g(\tau^*)} \quad (3)$$

where P—slag productivity of the smelt layer.

Determine the mass of melt in the bath:

$$M_b = N \cdot \rho_m \cdot \frac{\pi d_e^3}{6}.$$

Fuel consumption of experimental melting reactor is

$$B_{ng} = \frac{3600 \cdot W_n \cdot n_n \cdot 0.785 d_n^2}{\left(1 + \alpha v_{ox}^0\right)\beta_n}, \quad (4)$$

Here, n_n, d_n—number and diameter of nozzles, ∝—fuel consumption factor, v_{ox}^0—specific consumption of oxidant for complete combustion of fuel, and β_n− temperature coefficient of gas expansion in the nozzles.

The melt mixing time τ_{mix}, in the processing zone, is the most crucial factor influencing the melting reactor's performance.

The similarity equation is derived using the dimensions technique:

$$(\tau_{mix} \cdot g)/W_n = A(I_n/G_b)^k \cdot (W_n/W_{gr})^e \quad (5)$$

where I_n—gas flow momentum; G_b—melt bath weight; W_n—velocity of the gases in the purge grate's nozzles; and W_{gr}—gas velocity in relation to the purge grate's area, $(\tau_{mix} \cdot g)/W_n = H_o$—homochrony criterion.

The experiment's goal was to determine how the influencing factors affected the reactor's mixing time, within change $I_n/G_b = 0.09 - 0.42$ and $W_n/W_{gr} = 12 - 25$, according to the Equation (5). The method of experiment planning was used to generalize the experimental data. The experiment to ascertain the amounts from dependence (5) was conducted using linear experimental designs with variable factors at two stages. For this, Equation (6) was reduced to a linear form:

$$\lg H_o = \lg A + k\lg(I_n/G_b) + e\lg(W_n/W_{gr}) \quad (6)$$

$$y = b_o + b_1 \cdot x_1 + b_2 \cdot x_2 \quad (7)$$

The total number of factors is two, there are four experiments, and each experiment has three duplicate experiments. The significance of the regression coefficients was checked in comparison with the reproducibility error.

The adequacy of the regression equation was evaluated by Student's criterion with 95% confidence probability. After some transformation of Equation (7), the following similarity equation is obtained [24]:

$$H_o = \frac{\tau_{mix} \cdot g}{W_n} = 0.07(I_n/G_b)^{-0.6837}(W_n/W_{gr})^{0.0859} \quad (8)$$

which is fair within the range $I_n/G_b = 0.09 - 0.42$ and $W_n/W_{gr} = 12 - 25$.

Using the above method, the thermal characteristics of an industrial "melting reactor-rotary kiln" (MR-RK) model were calculated, some of which are presented in Figure 1.

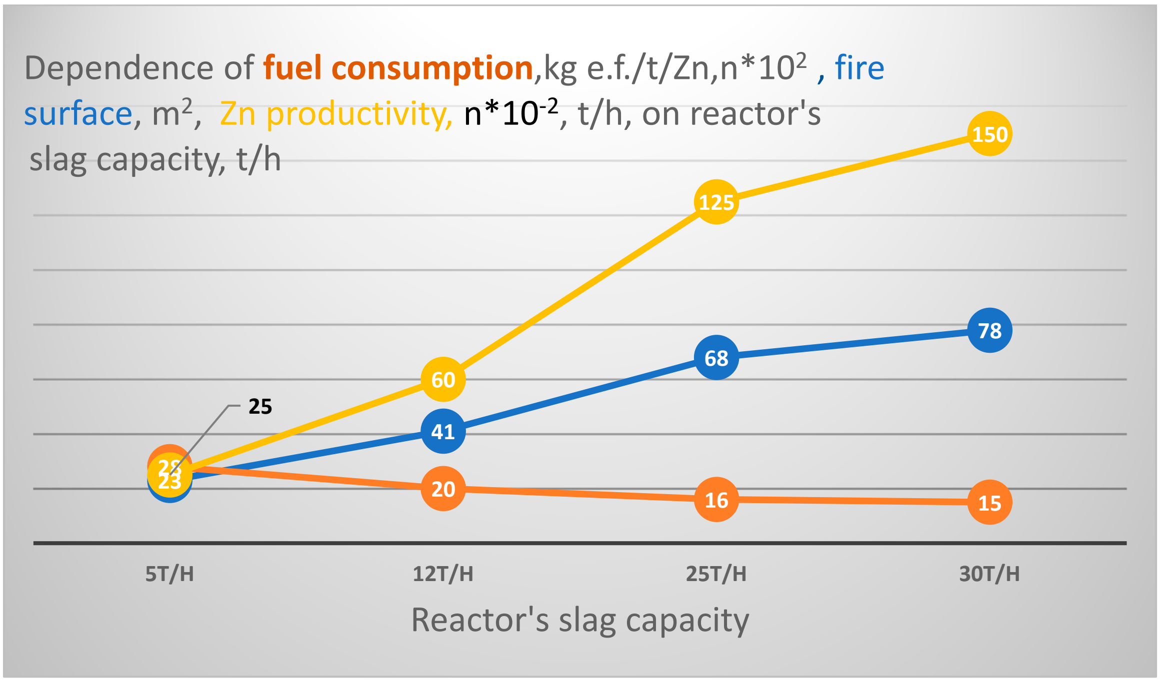

Figure 1. Dependence of specific equivalent fuel consumption, $n*10^2$ kg/tZn, fire surface, m^2, and Zn productivity, $n*10^{-2}$ t/h, on the reactor's slag capacity, t/h.

From Figure 1, we can conclude that enhancing productivity from 5 t/h to 30 t/h increases fire surface by 3.4 times and Zn productivity by 6 times, and it reduces the reactor's specific equivalent fuel consumption by 1.8 times.

For comparison, the size of a Waelz kiln for the production of zinc sublimates, for Leninogorsk polymetallic plant (LPP), is L = 70 m, D_{in} = 5.0 m, and V_{wk} = 1374 m^3, against the proposed "MR-RK"—640 m^3. Thus, the MR-RK unit has a processing volume (1374/640) $\approx$ 2 times less than Waelz kiln of LPP. When processing liquefied slag, with extraction degree E = 65–75%, at the Shimkent fuming furnace, the specific consumption of natural gas was 2400–2760 r.f/tZn. When processing granulated slag with E = 75–80% at the Waelz kiln of Leninogorsk polymetallic plant, with slag productivity 31 t/h, the specific consumption of reference fuel was 5800–6000 r.f/tZn. Thereby, in the MR-RK when processing slag, the specific consumption of reference fuel would be ~1.5 times less than slag treatment in the fuming furnace using melted slag and 3–4 times lower than Waelz–kiln processing of granulated slag [25].

4. Results of Experiments on Dump Slag

A pilot plant with a capacity of 1.5 t/h was built. Its general view is shown in Figure 2.

The operating principle of the pilot plant is as follows: Excavated slag from hoppers is continuously fed into the rotary kiln, where it is heated to 900 °C by waste gases of the melting reactor (MR) and routed into the same MR for slag melting, Zn distillation, and iron reduction. In the reactor's caissons, steam is generated. The exhaust gases from the rotary kiln are directed into the air heater to heat blast air to 500 °C. Gases, after being separated from zinc sublimates in the scrubber, are released into the atmosphere. After separating from iron, silicate slag is used for casting stone products.

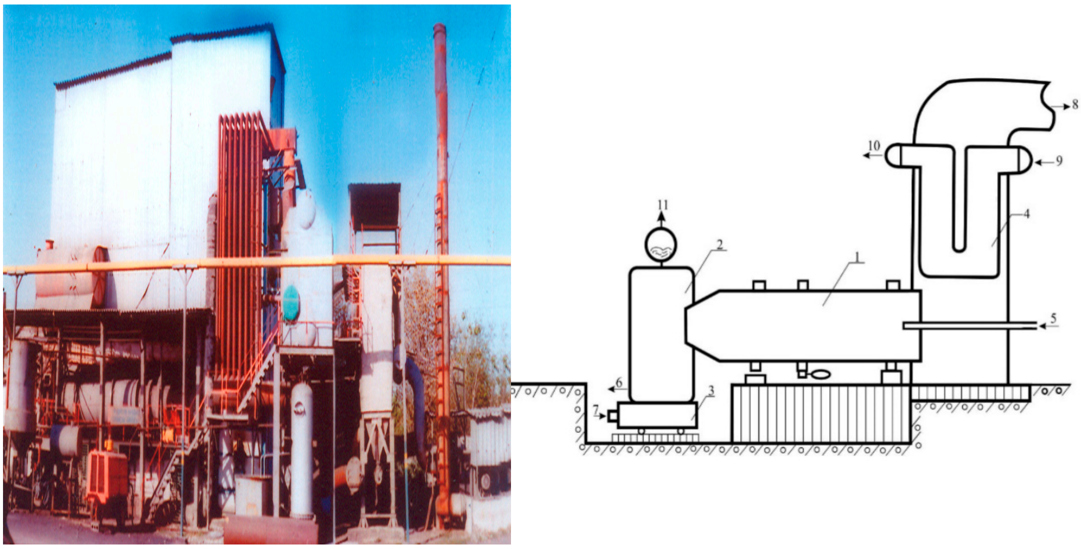

Figure 2. General view and principal scheme of the pilot plant. 1—rotary kiln, 2—melting reactor, 3—combustion chamber, 4—air heater, 5—air, 6—melt, 7—fuel, 8—off gases, 9—blast air, 10—hot air, and 11—steam.

During the period of experiments in the "smelting-reduction" mode, ~250 tons of "poor" slag with the following composition were processed: $ZnO(3.8–4.3)$; $PbO(0.1-0.15)$; $Cu(0.6-0.8)$; $FeO(7–8)$; $Fe_2O_3(2–3)$; $Fe_3O_4(23–24)$; $SiO_2(27–28)$; $CaO(13–14)$; $Al_2O_3(7–9)$; $S(0.4–0.5)$.

The melting reactor (MR) comprises a combusting chamber, purge grid, and smelting camera. (Figure 3). The operating principle of MR is as follows. Fuel and blowing air are supplied to the combustion chamber. Conversed gas comprising of reducing agents (CO and H_2), with a temperature of 1800–2000 °C, at a rate of 500–600 m/s, passes through a grid, and then is fed under the layer of smelt in the smelting chamber, for slag melting, Zn and Ge sublimation, and Fe reduction from oxides. Waste gases are directed into the rotary kiln.

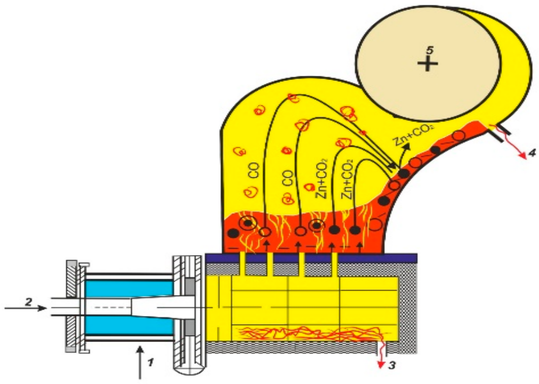

Figure 3. Principal scheme of the combustion chamber and melting camera. 1—air, 2—fuel, 3—ash-slag, 4—melt, and 5—gases.

The modes in the smelt layer are as follows:

(1) Bubble layer mode, within the purging intensity I_n/G_b = 0.036–0.09;
(2) "Ideal" mixing mode within $I_n/G_b = 0.091 - 0.19$;
(3) "Ideal" displacement mode within $I_n/G_b = 0.191 - 0.42$.

Here, I_n/G_b—ratio of the impulse of gases in the nozzles of the purge grid to the weight of the melt bath. $I_n = m_g \cdot W_n$, where m_g—mass flow of gases in the nozzles of the purge grid and W_n—gases velocity in the nozzle grid. $G_b = M_b \cdot g$, where M_b—mass of the melt bath in the reactor and g—gravity acceleration.

In contrast to the bubbling mode, where the layer structure has the form "liquid—continuous, gas—discrete" (Figure 4), the ideal mixing layer mode (Figure 5) is characterized by the state "gas—continuous, liquid–discrete".

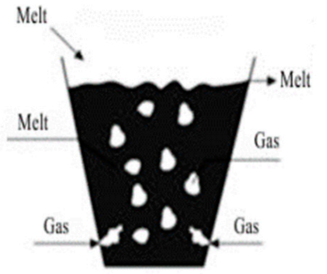

Figure 4. Bubble layer mode.

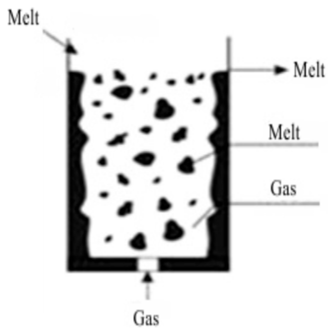

Figure 5. Ideal mixing layer mode.

The regimes for releasing the melt from a taphole are as follows (see Figure 6):

(1) From a vertical caisson (side exit);
(2) From the inclined caisson (frontal exit).

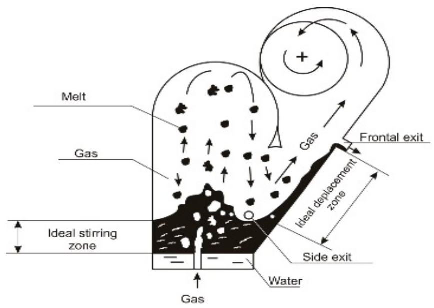

Figure 6. Ideal mixing–ideal displacement layer mode.

Thus, the average results of the experiments show the following:

(1) In bubble layer mode—I_n / G_b = 0.036–0.09, with the release of the melt from the vertical caisson (side exit), and zinc recovery does not exceed 30%;
(2) In the "ideal" mixing mode—$I_n / G_b = 0.091 - 0.19$, and in a mode beyond the "ideal" mixing—I_n / G_b =0.42, with the release of the melt from the vertical caisson (side exit), and the degree of zinc extraction is no more than 40%;
(3) In the "ideal" mixing–"ideal" displacement mode—$I_n / G_b = 0.19 - 0.42$, and only when the melt is released from the inclined caisson (frontal exit) does the zinc extraction degree reach 70%.

Table 1 shows the results of the experiments, where P—pilot plant productivity for slag, M_b—mass of the melt bath in the reactor, V_{O_2}—oxygen consumption, B_{ng}—natural gas consumption, W_e—electricity consumption, G_{st}—steam production, Zn^{in} and Zn^{fin}—initial and final zinc content in the slag, E—degree of zinc extraction, and "в"—specific consumption of natural gas per ton of zinc.

Table 1. Comparative experimental results.

	Melt Processing Methods	P, kg/h	M_b, kg	I_n/G_b	V_{O_2}, m^3/h	B_{ng}, m^3/h	Zn^{in}, %	Zn^{fin}, %	E, %	W_e kWh	G_{st} kg/h	b $\frac{m^3 ng}{tZn}$
1	Bubbling melt layer $I_n/G_b \leq 0.09$	1300	670	0.064	103	288	4.3	3.01	30	235	~1500	17,173
2	"Ideal" mixing layer I_n/G_b = 0.09–0.19	1336	400	0.099–0.26	108	305–319	4.3	2.32	42	230	~1500	12,640
3	Combination of the layer "ideal" mixing–"ideal" displacement" I_n/G_b = 0.19–0.42	1400	130	0.26	105	319	4.3	0.8	70	230	~1500	7272

The data in Table 1 demonstrate that when changing processing methods from a bubbling layer to a combination of the "ideal" mixing and "ideal" displacement layer, the degree of zinc sublimation "E" increases by 2.33 times, and the specific fuel consumption "b" decreases by 2.36 times.

Table 2 shows the characteristics of the measuring instruments.

Table 2. Measuring instruments and their characteristics.

Measured Value	Limit of Error	Name, Type, Serial Number	Measuring Range
Consumption of natural gas	At maximum gas flow—(±1)%, at minimum—(±2)%	Rotary gas meter, Delta, Munich, Germany, type 6250, serial number 7026904002.	From 0.8 m^3/h to 400 m^3/h
Flue gas temperature downstream of the rotary kiln, air heater, and scrubber	0.01 of measured medium temperature	Thermoelectric converters Metran, Ekaterinburg, Russia. Type TXA-0292K, 4 pcs.	From (−400 °C) to (+1000 °C)
The pressure of natural gas and blast air in front of the furnace	From (±0.25)% to (±0.5)%	Overpressure sensors Sapphire 22M-DI, Ekaterinburg, Russia, model 2140, 2 pcs.	0~250 kPa
The composition of the combustion products behind the reactor, rotary kiln, air heater, and scrubber	From (±5%) to (±1%)	Manual automatic gas analyzer with display and printer, "TEMPEST 100" from Telegan, Antverpen, Belgium.	CO_2-(0.0÷15%); CO-(0.0–15%); O_2(0–30%)800 °C
Melt temperature in the melting reactor	±3°C	Optical pyrometer "Smotrych", Ekaterinburg, Russia. No. 6792.	From 800 °C to 5000 °C

5. Results of Experiments on the Clinker

The process of iron recovery from Achisai clinker, in the MR-RK unit, had the following characteristics: slag capacity of 1000 kg/h; natural gas consumption—600 m^3/h; coke dust—160 kg/h; combustion air—1400 m^3/h; oxygen—430 m^3/h; electric power—400 kWh; discharge correction factor of oxidizer—0.4; and calorific capacity of gas beyond the rotary kiln—7000–7500 kJ/m^3. The chemical composition of the obtained silicate slag is as follows, in %: SiO_2 (42–44); Al_2O_3 (12–13); Fe_2O_3+FeO (9–10); CaO (22–23); MgO (5–6); MnO (0.5–0.7); Na_2O (2.0–2.5); Zn (0.8–1.0); Pb (0.02–0.03); and S (0.15–0.17).

Figure 7 demonstrates smelt release from the inclined caisson and the garnissage lining in the reactor, respectively.

Figure 7. Ideal mixing–ideal displacement layer mode.

During the process of pouring the melt into molds, at 1300 °C, the samples quickly solidified in ambient at a temperature of 850–900 °C. Gold and silver particles scattered throughout the melt act as catalysts for crystallization, promoting intensive solidification of the samples. Exposure in a muffle furnace at a temperature of 900% for 5–10 min leads to complete volumetric crystallization of the samples. Table 3 shows the physicochemical characteristics of stone casting samples.

Table 3. Melting mode and properties of stone casting samples.

1	Melt temperature at the exit from the tap hole, °C	1300–1350
2	Melt viscosity, poise	9–10
3	Specific heat flux through water-cooled reactor caissons, kW/m^2	120–130
4	Density, g/cm^3	2.9–3.0
5	Water absorption,%	0.16
6	Compressive strength, kgf/cm^2	2500
7	Abrasion loss, g/cm^2	0.11–0.23
8	Softening temperature, °C	1000
9	Acid resistance in hydrochloric acid, %	97.7
10	Grain (crystal) size, microns	60–150
11	Heat resistance, heat changes	18–20

Thus, it has been experimentally proven that when iron is extracted from clinker with a residual amount of 9–10%, the composition of the clinker automatically becomes suitable for casting stone products.

Discussion of Experimental Results

During the experiments, when releasing the melt from a vertical caisson (side exit), in the bubbling layer mode with $I_n/G_b = 0.091$, layer of "ideal" mixing with I_n/G_b = 0.09–0.19, and outside the layer "ideal" mixing with I_n/G_b =0.42, zinc recovery rate did not increase above E = 40%. Since the release of the melt from the vertical caisson, in the above blowing ranges, is determined by the ideal mixing regime, it can be concluded from this that the possibility of increasing zinc extraction in the "ideal" mixing layer, only by increasing the blowing intensity, has a certain limit due to internal physicochemical processes. After conducting experiments with the release of the melt from the inclined part of the reactor, from the frontal exit (let us call it the ideal displacement mode), with the same value of I_n/G_b = 0.42, a satisfactory value of the degree of zinc sublimation was achieved—E = 70%. Thus, a natural question arises for the experimenter: What is the role of the inclined caisson in increasing the degree of zinc recovery?

Dump slag contains complex compounds of Zn, such as zinc silicate (Zn_2SiO_4), zinc ferrite ($ZnFe_2O_4$), and so on. Before recovering zinc from such complex compounds, they will need to be decomposed into simple molecules (see Table 4, points 1 and 2), and then, the zinc will only be sublimated into the gas phase (see Table 4, point 3).

Table 4. Thermodynamic characteristics of reactions at t = 1500 °C [26].

	Reactions	ΔG, kJ	K
1	$Zn_2SiO_4 = 2ZnO + SiO_2$	36.203	0.086
2	$ZnFe_2O_4 = ZnO + Fe_2O_3$	33.426	0.103
3	$ZnO + CO = Zn_g + CO_2$	−20.959	4.145
4	$2ZnO + SiO_2 = Zn_2SiO_4$	–36.20373	11.662
5	$ZnO + Fe_2O_3 = ZnFe_2O_4$	–33.426	9.656

As follows from Table 4, the nature of the change in the Gibbs energy of formation of complex molecules Zn_2SiO_4 и $ZnFe_2O_4$ from simple ones, ZnO, SiO_2, and Fe_2O_3 negative, and the nature of the change in the Gibbs energy for the silicate (Zn_2SiO_4) and zinc ferrite ($ZnFe_2O_4$) decomposition reaction to these simple components (ZnO, SiO_2, and Fe_2O_3) is positive. The average value of the equilibrium constant (K) for the reaction of the formation of complex molecules from simple components (Table 4, points 4 and 5) is roughly 100 times greater than the reaction that occurs when complex molecules break down into simpler ones (Table 4, points 1 and 2). Therefore, it is more likely to be expected that in the "ideal" mixing mode, two reactions opposite in direction take place in the melt layer: (1) the reaction of the decomposition of complex molecules into simple components and (2) the reaction of the formation of complex molecules from simple components. From the latter, it can be stated that in the above "ideal" mixing modes (I_n/G_b = 0.091, I_n/G_b = 0.42), with the release of the melt from a vertical caisson (side exit), due to rearrangement between recombined molecules ZnO, SiO_2, and Fe_2O_3 with the re-formation of zinc silicates and zinc ferrites (Zn_2SiO_4 and $ZnFe_2O_4$), no increase in zinc extraction was observed.

The process of removing the melt from the reactor's inclined caisson (frontal exit) was formerly referred to as the "ideal" displacement mode. Since in the inclined layer of the melt, there is "ideal" displacement (see Figure 6), the process of the decomposition of complex molecules is also underway and each elementary stream in it moves parallel to the other; then, the probability of the mixing of the recombined molecules, ZnO, SiO_2, and Fe_2O_3, and accordingly, the formation of complex components, Zn_2SiO_4 and $ZnFe_2O_4$, from them, decreases, and the degree of zinc reduction according to the formula $ZnO + CO = Zn_g + CO_2$ increases.

Thus, the results of the experiments show that zinc extraction increases only when the hydrodynamic regime in the melt bath passes from the "ideal" mixing mode to a combination of the "ideal" mixing and "ideal" displacement modes.

6. Development of an Environmentally Friendly Slag-Processing Thermal Diagram

The problem of reducing the emissions of harmful gases has been the subject of many works [27–31]. In this article, the authors propose a new version of the neutralization of CO_2 and other gases [32].

Based on the zinc method of CO_2 decarbonization, a thermal diagram of an energy-saving, waste-free, and environmentally friendly system for processing dump slag and clinker was developed (Figure 8). The acting principle of the system is as follows. The charge, consisting of dump slag (clinker), Ekibastuz coal, and limestone, is loaded into rotary kiln 1, where it is heated by the melting reactor's (MR 2) waste gases. Then, in the stream of air, the charge is blown into the same MR 2. Ekibastuz coal contains ~200 g/t of gallium and germanium. In the MR, the charge is melted, zinc and germanium are sublimated from it, and the silicate melt is sent to the production of building materials. The oxidizer is oxygen-enriched air. Condensed zinc from the electrothermal distiller, 3, in the stream of steam, is dispersed into the intertube space of the air heater (AH), 4. In 4, the main reactions take place—Zn + H_2O = ZnO + H_2 and Zn + CO_2 = ZnO + CO. Waste gases containing H_2, CO, and ZnO pass through economizer 5, where the substitution reaction CO + H_2 = C + H_2O occurs, with the release of atomic carbon (soot). Further, gases from chamber 5, consisting of H_2O, C, and ZnO, enter the electrostatic precipitator 6 to separate soot (C) and ZnO sublimates from gases. Effluent gases containing mainly water vapor and nitrogen, with leftover CO_2, are released into the atmosphere. A mixture of soot (C) and sublimates (ZnO, Ga_2O_3, and GeO) is sent to the "distiller" 3, the main products of which are condensed zinc, CO gas containing a pusier (blue powder), and sublimates of Ga_2O_3 and GeO. CO gas from the condenser, after being cleaned from pusier, and sublimates of gallium and germanium in bag filters 7, is sent to the MR 2 as additional fuel.

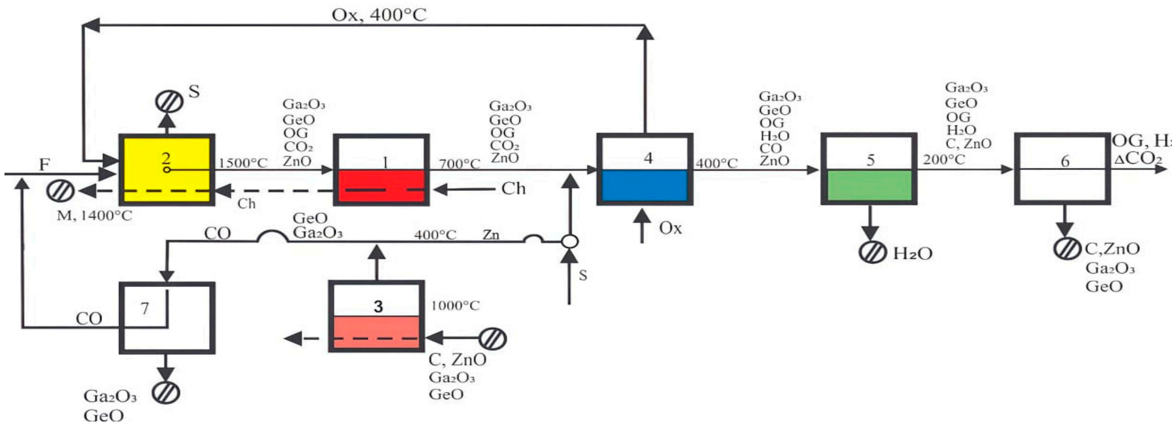

Figure 8. Proposed thermal diagram of energy-saving and environmentally safe processing of dump slag and clinker. 1—rotary kiln, 2—melting reactor, 3—zinc distiller, 4—air heater, 5—economizer, 6—electrostatic precipitator, 7—bag filters. Ch—charge, M—silicate melt, F—fuel, Ox—oxidizer, S—steam, OG—outgoing gases, C, CO, CO_2, and H_2O—carbon, carbon monoxide and carbon dioxide, and water vapor, respectively, and Zn, ZnO, Ga_2O_3, and GeO—condensed zinc, sublimates of zinc, gallium, and germanium, respectively.

Thus, if the proposed system is implemented, along with waste-free slag processing, the following will occur: the neutralization of carbon dioxide and nitrogen oxides reduction by hydrogen in the process, and the binding of sulfur with the CaO, subsequently eliminating the appearance of sulfurous gases.

The economic efficiency of the suggested installation is calculated, and the findings are shown in Table 5.

Table 5. Findings of calculations of the payback period of an investment for an installation with a capacity of 25 t/h for clinker.

When Producing Only Zinc Sublimates (Pessimistic Scenario)			**At the Production of Zinc Sublimates and Stone-Casting Products (Optimistic Scenario)**		
Product price Cp*r*, USD/y	Payback period τ, years	Expected net profit, USD/y	Product price Cpr, USD/y	Payback period τ, years	Expected net profit, USD/y
10,189,274	4.64	4,466,039	16,186,428	2.24	9,263,762

Thus, according to Table 5, the payback period for an installation with a capacity of 25 t/h for clinker would be, when producing only zinc sublimates, 4.64 years, and in the case of zinc sublimates and stone-casting production, it would be 2.24 years.

A zinc extraction ratio of 70% from clinker will yield about 157,000 tons of zinc sublimates in total. The lowest market potential for Achisai dump clinker would be around USD 125,600,000 if the cost of commercial clinker sublimates is USD 800/t.

Capital expenditures K = USD 20,714,525; production cost C_{pr} = USD 4,606,725/y; and the price of stone cast slabs is USD 54/t, where $\tau = \frac{K}{(Ppr - Cpr)\cdot 0.8}$.

7. Conclusions

The Republic of Kazakhstan's mining and metallurgical industry dumps contain about 17 billion tons of waste. Only at the metallurgical workshop of the Achisai mine, about 4.5 million tons of clinker with ~USD 125,600,000 market potential has been accumulated. However, the extraction of metals from clinker requires 2–3 times more specific energy than their production from rich ores, which involves the development of energy-saving technology for their cost-effective processing. To solve the problem, a "melting reactor–rotary kiln" with a 1.5 t/h slag productivity was built. The following conclusions were drawn from the experiment results:

1. In the bubble layer mode (I_n/G_b = 0.036–0.09), the "ideal" mixing mode (I_n/G_b = 0.091–0.19), and beyond the "ideal" mixing mode, (I_n/G_b = 0.42), with the release of the melt from the vertical caisson, the degree of zinc extraction is no more than 40%; the latter proves that only with an increase in the intensity of purging is it impossible to increase the extraction of zinc and, accordingly, reduce the specific fuel consumption.
2. In the melt layer, two reactions opposite in direction and intensity were discovered, slow reactions of decomposition of complex components (Zn_2SiO_4, $ZnFe_2O_4$) into simple molecules (ZnO, SiO_2, Fe_2O_3) and rapid reactions of the formation of complex components from simple molecules; since in the inclined layer of the melt, there is "ideal" displacement, the process of decomposition of complex molecules is also underway and each elementary stream in it moves parallel to each other, then the probability of the mixing of recombined molecules, ZnO, SiO_2, and Fe_2O_3, and accordingly, the formation of complex components, Zn_2SiO_4 and $ZnFe_2O_4$, from them decreases, and the degree of zinc reduction according to the formula $ZnO + CO = Zn_g + CO_2$ increases. In the "ideal" mixing–"ideal" displacement mode ($I_n/G_b = 0.19 - 0.42$), and only when the melt is released from the inclined surface, the zinc extraction degree reaches 70%; at the same time, the degree of zinc sublimation increases by 2.33 times, and the specific fuel consumption decreases by 2.36 times. A new phenomenon has been found by the last, which we have named a combination of "ideal" mixing and "ideal" displacement modes.
3. In traditional processes for processing zinc-rich slag, for example, by fuming or Waeltzing, the waste slag was thrown into a dump due to its unsuitability for the production of building material. In the experiments, after reducing and separating the iron, during the pouring of the melt into molds, at 1300 °C, the samples quickly solidified in ambient between 850 and 900 degrees Celsius; gold and silver particles scattered throughout the melt act as catalysts for crystallization, promoting intensive solidification of the samples; and exposure in a muffle furnace at a temperature of 900 °C for 5—10 min leads to complete volumetric crystallization of the samples. Thus, the novelty of the work is the production of a melt suitable for stone casting when clinker is depleted of iron, with a residual iron content of 9–10%; the latter also contributes to the reduction in specific fuel consumption for the process.
4. The melting reactor based on a combination of the "ideal" mixing and "ideal" displacement methods is also new; experiments carried out for the processing of ~250 tons of "poor" slag showed the structural reliability of the unit. According to the experiment results while processing the slag, the specific fuel consumption in the reactor inversion

phase would be approximately 1.5 times lower than when utilizing molten slag in the fuming furnace and 3–4 times lower than when processing granulated slag in Waelz kiln.

5. Based on the zinc method neutralization of CO_2, a thermal diagram of an energy-saving, waste-free, and environmentally friendly system for processing dump slags and clinker was developed. Implementation of the proposed system ensures the neutralization of carbon dioxide and nitrogen oxides by hydrogen and the binding of sulfur with the CaO, subsequently eliminating the appearance of sulfurous gases.
6. To predict the characteristics of an industrial sample of the melting unit, the affine modeling method was used; recalculating fuel consumption from a pilot plant with a 1.5 t/h clinker (slag) capacity to an industrial sample with a 25 t/h capacity revealed that, under a pessimistic estimate, the investment payback period would be between 4 and 5 years.

8. Prospects

Currently, an experimental reactor inversion phase is being built for the energy-saving processing of power plants' ash slags, tin ores, and phosphorus-containing waste.

The authors plan to commercialize the smelting unit "reactor inversion phase—a rotary kiln" for non-waste, extracting all the valuable components contained in the technogenic waste of Kazakhstan.

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Nomenclature

M	flow of substance mass (kg);
β	mass-transfer coefficient in the melt (m/s);
F	total surface of mass transfer (m^2);
ΔC	gradient of impurities concentration at the boundary of phases (kg/m^3);
τ	dwelling time of bubbles in the melt (s);
θ	particle's medium volumetric dimensionless concentration of ZnO;
C_{in}, C_f	initial and final particle concentration of the zinc in the melt;
τ_{stir}	melt stirring time in the processing zone;
H_o	homochrony criterion;
K	reaction's equilibrium constant, –;
ΔG	change in Gibbs (free) energy (kJ);
I^n/G_b	ratio of the momentum of gases in the nozzles of the purge grate to the weight of the reactor's bath, –;
W_n/W_g	ratio of the nozzle and purge grate gas velocities, –;
M_b	mass of the reactor inversion phase bath (kg);
P	reactor's capacity (kg/h).

Acronyms

MR-RK	melting reactor-rotary kiln;
LPP	Leninogorsk polymetallic plant;
AH	air heater.

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