Studies of the Possibility of Improving the Quality of Iron Ores and Processing of Technogenic Composite Iron-Containing Waste of Metallurgical Production

Dauren Yessengaliev [1], Marzhan Mukhametkhan [2,*], Yerlan Mukhametkhan [2], Gulnara Zhabalova [2], Bauyrzhan Kelamanov [1], Olga Kolesnikova [3,*], Bakhytzhan Shyngysbayev [4], Laura Aikozova [5], Kuralay Kaskataeva [6] and Yerbol Kuatbay [7,*]

[1] Department of Metallurgy and Mining, K. Zhubanov Aktobe Regional University, Aktobe 030000, Kazakhstan; dauralga@mail.ru (D.Y.); kelamanov-b@mail.ru (B.K.)

[2] Department of Metallurgy and Materials Science, Karaganda Industrial University, Temirtau 101400, Kazakhstan; livereke@gmail.com (Y.M.); g-zhabalova@mail.ru (G.Z.)

[3] Department of Science, Production and Innovation, M. Auezov South Kazakhstan University, Shymkent 160012, Kazakhstan

[4] Department of Natural Sciences, Shymkent University, Shymkent 160031, Kazakhstan; shingis63@mail.ru

[5] Department of Chemistry and Pharmaceutical Engineering, M. Auezov South Kazakhstan University, Shymkent 160012, Kazakhstan; laura.aykozova@mail.ru

[6] Department of Geology and Exploration of Mineral Deposits, Karaganda Technical University Named after Abylkas Saginov, Karaganda 100026, Kazakhstan; aigakk@mail.ru

[7] Department of Metal forming, Karaganda Industrial University, Temirtau 101400, Kazakhstan

* Correspondence: marzhan_mukhametkhan@mail.ru (M.M.); ogkolesnikova@yandex.kz (O.K.); kazakh_84@mail.ru (Y.K.); Tel.: +7-(747)-459-81-19 (M.M.)

Abstract: Ferrous metallurgy has been and remains one of the main types of production activities that enables humanity to extract, process and produce basic equipment for all types of activities. The growth of ore production as well as the reduction in world reserves of the raw material base have lead to the search for effective methods of processing and preparation of waste for metallurgical processing. The mining and metallurgical sector of the Republic of Kazakhstan, which has its an integrated mining and metallurgical complex with its own coal, iron ore, and energy base, uses iron ores from several deposits. It also includes ash and sludge storage tanks, which store valuable metallurgical waste, such as converter production sludge, rolling scale, and others, the use of which is hindered by the presence of certain harmful impurities in the composition (a rather high content of non-ferrous metals, especially zinc, a high content of oils, etc.). These valuable technological wastes require additional research that may contribute to their use as a charge or as iron-containing components of the charge. Based on the urgency of the tasks of dephosphorylation of iron ores and utilization of human-made waste (converter sludge and rolling scale), studies were conducted to try to eliminate existing problems. The results of the research work make it possible to obtain metals based on prepared pellets with a significantly low phosphorus content; this will enable the use of an oiled rolling scale and converter sludge for the production of a metalized product for steel smelting. The resulting metalized products make it possible to dispose of scale and converter sludge by 70%, and the degree of iron extraction exceeds existing methods by 1–3.5% (92.1–94% vs. 95.6%).

Keywords: composite iron-containing waste; sludge; dephosphorization; environmental; engineering; iron ore concentrate; metalized product; sediment

1. Introduction

The improvement of the ferrous metallurgy industry is one of the main requirements for the production of technological equipment in all sectors of the national economy. The growth of metal smelting implies the improvement of the raw material base by increasing

the productivity of existing and mastering new iron ore mining enterprises. The open-pit mining method, the share of which already exceeds approximately 90% in iron ore production, will remain predominant in the future. Technical re-equipment of quarries with new drilling equipment and automated special equipment will also be developed.

At the moment, the reserves of iron ore in Kazakhstan amount to l6.6 billion tons, which corresponds to approximately 8% of all world reserves, of which approximately 8800 million tons have been explored and prepared for operation. Approximately 90% of iron ore is concentrated in the Torgai region of Northern Kazakhstan, the rest is located in Central Kazakhstan [1].

Several iron ore deposits with approved reserves of over 6 billion tons are exploited in the republic [2]:

- Sokolov-Sarbay (SSMPPA, Rudny, Kazakhstan) (including Kachary) with approved reserves of more than 2500 million tons; iron content—38–43%; harmful admixture—sulfur;
- Lisakov (LGOK) (Lisakovsk, Kazakhstan), approved reserves—more than 3000 million tons; iron content—3438%; harmful admixture—phosphorus;
- Atasuy (Zhanaarka, Kazakhstan), approved reserves—more than 800 million tons; iron content—48–70%; harmful admixture—sulfur;
- Atansor (Birzhan Sal, Kazakhstan), approved reserves—more than 39 million tons; iron content—37–57%; no harmful impurities.

Currently, ArcelorMittal Temirtau JSC uses a charge from unfavorable iron ore raw materials characterized by a complex composition for smelting pig iron:

- Pellets and SSMPPA concentrates with high sulfur content and low mechanical strength;
- Lisakov concentrates with high (up to 0.8%) phosphorus content and low iron content;
- Atasui (Zhanaarka, Kazakhstan) unenforced ferromanganese ores having a low iron content (less than 48.0%), an increased content of manganese and sulfur;
- Kentobe (Karkaralinsk, Kazakhstan) unenforced magnetite ores with a high (up to 3.5%) sulfur content.

Unenforced ores are currently being mined by selective extraction, which may soon remove the Atasu, Atansor, Kentobe, and Balbrown deposits from the active balance.

Uncompetitive iron ore concentrate of the Lisakov deposit (iron content—49.2%, phosphorus—0.7%, alumina ~5%) is supplied to ArcelorMittal Temirtau JSC in a limited volume (approximately l.5 million tons per year) [3].

In other respects, due to the orientation of the EPA to the Chinese and Russian markets with a rapid overestimation of the price of concentrate and pellets purchased from this plant, ArcelorMittal Temirtau JSC is forced to finally switch to the use of Lisakov ores. Ores from other deposits of the republic are delivered to JSC "ArcelorMittal Temirtau" in raw form, without enrichment (only their grinding is used), since there are no processing plants at proper enterprises (commercial). The main difficulties of the iron ore complex of Kazakhstan are as follows:

- Depletion of the prepared reserves of the main mines;
- High degree of wear of technological equipment, building structures, industrial buildings, structures;
- Lack of effective iron ore processing technology that enables complex processing of raw materials;
- Imperfection of the technology of enrichment of raw materials and its high energy intensity;
- Insufficient investments for the development of existing and preparation of new fields and technical re-equipment.

JSC "Sokolov-Sarbay Mining and Processing Production Association" (SSMPPA) (Rudny, Kazakhstan). The association includes Sarbay, Sokolov, Kachary, Kunzhulsk, and Sokolov operating quarries, an underground mine. Main directions: production of iron ore concentrate, fluxed pellets, extraction of crude crushed ore, dolomite, limestone,

and crushed stone. The products of JSC "SSMPPA" are of high quality, with an iron content of more than 66% in concentrate and over 62% in pellets. The main importers of the plant's products are Magnitogorsk Iron and Steel Works JSC (Magnitogorsk, Russia) (up to 70%) and ArcelorMittal Temirtau JSC (30%).

Lisakov iron ore deposit is located in the Kostanay region (Republic of Kazakhstan). The development of the Lisakov deposit is carried out openly on small horizons, without the use of drilling and blasting operations, which ensures the lowest cost of ore. The bulk of the ore is represented by a fine-grained oolite variety. The main ore mineral is hydrogenated.

The deposit has been produced since 1970. Based on its base, a mining and processing plant is founded and operates, the production of which is a gravity-magnetic concentrate with an iron content of 39–40%. Such a concentrate acquires a fraction of less than 1 mm and contains 0.8–0.9% phosphorus, which suppresses its use in metallurgical processing. In the case of blast furnace smelting, phosphorus completely passes into cast iron. Phosphorus removal in steelmaking involves double loading of slag and is economically unacceptable. Removal of phosphorus from cast iron in buckets also remains a problematic operation that requires a lot of money. As a result, almost all the efforts of scientists are aimed at finding a technology that enables removing phosphorus from Lisakov concentrate at the stage of ore preparation for blast furnace conversion [4–8].

There are hydrometallurgical methods for the treatment of phosphorus from iron ores [9,10]. In one method, soda solutions are used, in another ore is treated with an alkali solution, in the third with a hydrochloric acid solution. Spanish and French scientists proposed leaching phosphorus with sulfuric acid at room temperature. The disadvantage of this technology is the long (5–25 h) duration of leaching. Australian researchers proposed to carry out preliminary heat treatment at a temperature of 500–600 °C for 1.0–1.5 h before phosphorus leaching, and subsequent leaching with sulfuric acid at a temperature of 60–80 °C for 2–3 h. The disadvantage of this technology was the low extraction of phosphorus into the solution.

Russian researchers [11] proposed to carry out preliminary heat treatment of the concentrate at a temperature of 800–1000 °C for 1 h, and the subsequent leaching of phosphorus from the burnt concentrate with sulfuric acid at a temperature of 20–50 °C and the ratio solid:liquid = 1:(1–2). This technology has significant disadvantages that make it difficult to implement it on an industrial scale. The optimal firing temperature of the concentrate is not clear from the presented data. There is no indicator of the quality of firing, according to which it would be possible to adjust the firing mode and control it. The optimal firing duration is not clear. In the technology under consideration, phosphorus is leached with sulfuric acid with a high concentration (49%) and the question of the optimal concentration of sulfuric acid remains unclear. This technology does not answer the questions of mutual optimization of the parameters of firing and leaching, as well as the mechanisms of these conversions themselves.

Belgian researchers proposed to carry out preliminary roasting with the addition of alkali with the formation of water-soluble phosphates and subsequent water leaching [12], which requires a significant consumption of alkali.

In the Kazakh patent [13], clarifications were made to the Russian patent discussed above: the pre-firing temperature of the concentrate is 1000–1200 °C. Such a Kazakh patent is practically unrealizable since at these temperatures, the concentrate is sintered and the technological regime in the firing unit is completely upset. In another Kazakh patent [14], it is proposed to carry out acoustic or radiation treatment of the concentrate before firing, due to which, according to the developers, it is possible to reduce the firing temperature.

Russian researchers [15] proposed firing the concentrate in a reducing medium at a temperature of 1350–1450 °C. Under these conditions, specks will form and the industrial implementation of such a process is unlikely.

Considering the insufficiently developed mechanisms of firing and leaching, as well as the shortcomings of the proposed technologies, JSC VNIIMT (Yekaterinburg, Russia)

conducted initiative studies of pyro-hydrometallurgical technology of dephosphorization of Lisakov concentrate using firing and leaching with sulfuric acid.

The main feature of this dephosphorization technology is the ability of phosphorus to leach after firing at temperatures of 800–1000 °C, which is associated with the crystal-chemical transformation of a phosphorus-containing component containing high-temperature hydrated moisture in the initial concentrate. The ability of phosphorus to leach appears only when the hydrated phosphorus-containing component decomposes with the release of hydrated moisture.

The kinetics of high-temperature dehydration of Lisakov concentrate was studied by thermometric method on a NETZSCH STA 449 C Jupiter device, which enables continuously determining the change in the mass of the sample in grams with an accuracy of up to the fourth decimal place when the temperature changes. At the same time, the thermal effects occurring when the sample is heated are determined by differential scanning calorimetry.

The authors [16] believe that the formation of cracks on Lisakov concentrate particles during high-temperature firing is due to high stresses arising in the particle due to a sharp reduction in the molar volume of the initial hydrogenated substance during its transition to hematite with simultaneous segregation of phosphorus at the grain boundary. However, it should be noted that the change in the crystal lattice during the transition of hydrogenated hematite occurs at a temperature of 300–350 °C, with the release of hydrate moisture associated with iron, and at the same time cracks on the particles are not formed.

The increase in the accumulation of human-made waste, the continuous increase in the prices of energy resources and charge materials, and the tightening of environmental regulations entail the need to find effective and economically justified methods and technologies for processing and recycling of metallurgical waste. Excessive moisture and petroleum products in the composition of rolling scale complicate their use as a charge in metallurgical processing. The problem of utilization and recycling of converter sludge is very relevant, since ensuring the elimination of these problems, implies solving several important tasks: providing the enterprise with iron-containing raw materials, solving environmental problems of utilization of fine waste [17], helping to save natural raw materials and reduce the cost of steel produced [18]. In this regard, the use of efficient recycling technologies is one of the urgent tasks of modern metallurgy.

Analysis of data on waste disposal of JSC "ArcelorMittal Temirtau" shows that almost 2 tons of waste is generated for every ton of finished rolled products. More than 130 million tons of sludge, coal processing waste, ash, slag, and other products of metallurgical processing of mineral raw materials and fuel have been accumulated in dumps and tailings dumps. Annually, in the current conditions of recycling, almost 5 million tons are added to them (more than 1 ton per ton of finished rolled products) [19].

Waste from metallurgical production belongs to Class III—moderately hazardous substances. They have an average degree of harmful impact on the environment. They still lead to a violation of the ecological system, but it takes approximately 10 years to restore. After that, the influence of the source of infection is reduced to a minimum. This hazard class includes compounds of manganese, silver, nickel, copper, benzene-containing waste, hydrochloric acid, trichloroethylene, phosphates, ethyl alcohol, and other substances.

Rolling scale is formed as a result of secondary oxidation of the metal surface layer when heated before rolling. When 1 ton of steel is heated, approximately 25–30 kg of scale is formed (2.5–3.0%) [20]. Up to 50 million tons of rolling ore are produced annually in the world, up to 1 million tons in Kazakhstan. Rolling scale is most widely used in agglomeration production as an iron-containing component of the sinter charge.

For the successful use of the scale of rolling production as a valuable secondary raw material in metallurgy, technologies are needed to remove oil and moisture from the scale.

Even though for a long time abroad and in our country, the technology of de-oiling of scale has been developed and some of these technologies have been implemented on an industrial scale, the presence of growing volumes of dumps of oiled scale indicates that

there is still no effective way to process it, although a wide range of technologies based on chemical, mechanical, biochemical and thermal methods.

So, for example, for the mechanical method of scale de-oiling, the obstacle is the strong abrasive wear of the apparatus components, oiling and clogging of the filter cloth, and the impossibility of its regeneration.

In technologies of scale de-oiling by flotation and centrifuges, it is not possible to obtain a solid phase of scale with an oil content of less than 4–5%; therefore, it is subjected to further processing [20].

At the moment there are several stages of technological handling of rolling scale:

The first stage is primary settling tanks. This scale contains up to 1.74–3.8% of oils. From the primary settling tank, the scale is shipped by a grab crane to the wagons.

The second stage is secondary settling tanks. After the primary settling tanks, water with fine-scale particles (less than 0.1 mm) enters the intermediate pumping station, and from it is pressurized to the secondary settling tanks. As a rule, these are multi-section horizontal settling tanks. An oil removal system is provided on the sump. The scale of secondary settling tanks contains more petroleum products and water, making it difficult to prepare and dispose of them. For this reason, this material is disposed of on average by only 75.1%. The scale from the sump is taken away by a grab crane. Part of the larger scale is taken from the pockets of the sections and stored on a special platform for drying. As the wagons arrive, it is shipped to consumers. The content of petroleum products on this scale is 1.8%. The other part of the smaller scale with a content of petroleum products up to 15% is stored in a concrete bunker and periodically exported to the dump.

The main method of using a scale is the use as an iron-containing component of the charge in agglomeration production.

Experiments on the use of an oiled scale from the settling tanks of the Kryvorozhstal combine (JSC ArcelorMittal Kryvyi Rih, Kryvyi Rih, Ukraine) in the charge for the production of pellets were carried out at the Central GOK. The oil and moisture content in the scale was 20% each. Oiled scale mixed with limestone and bentonite was crushed in ball-ventilated mills with a coolant. The quality indicators of the fired pellets when using a flux mixture with the addition of an oiled scale remained practically unchanged [21].

The paper in [22] presents the results of laboratory studies on obtaining metalized materials from a mixture of oiled scale with activated peat by heat treatment of this mixture at temperatures of 1150 and 1250 °C in metal containers. With a carbon content of 6% in the mixture, the achieved degree of scale metallization was 20 and 43%, respectively. The degree of metallization increased with increasing heat treatment time.

In other experiments, a mixture of oiled scale with activated peat was subjected to heat treatment on a grate with products of steam conversion of natural gas. At the maximum peat content in the mixture and a heat treatment temperature of 1150 °C, 100% degree of metallization was achieved. In similar experiments with an oiled scale without peat, the degree of metallization of the resulting product did not exceed 15% [23,24].

The second group includes technologies for the disposal of fine dispersed iron-zinc-containing waste subjected to mixing and after oxidation with carbon-containing material. first of all, these are technologies for the metallization of waste in annular chamber furnaces with a rotating hearth and in a multi-hearth furnace Primus [25–29].

The Inmet process was developed by the International Nickel Company (INCO) (Toronto, Canada) in 1970. After successful testing of the process, an industrial unit was built at a pilot plant in Elwood City (PA, USA), which began operating in 1978. The process of the reduction of Fe, Zn, and Pb is carried out in a stationary layer of ore pellets on a moving hearth in a chamber furnace.

A similar DRyIron process was developed by Aum Research and Engineering based on the developments of Midland Ross. DRyIron technology plants are built by: AmerSteel in Jackson (TN, USA), Rouge Steel in Dearborn (Wayne County, MI, USA), and Nippon Steel Corp. in Hikari (Japan) [25].

The Comet process was developed in the laboratories of the Metallurgical Research Center (CRM) in Belgium with the participation of Paul Wurth (Luxembourg). However, no industrial installations are operating by this method [30].

The third group should include new, unconventional methods of processing substandard iron-containing materials by blowing the composition of combined mixtures into blast furnaces and electric arc furnaces, characterized by simplicity, small investments, and aimed at maximizing the reduction in harmful emissions and environmental pollution.

Analysis of the results of research in this direction by specialists from Germany, France, Japan, etc., performed in laboratory conditions, on hot stands, and experimental blast furnaces, also by computer modeling of blast furnace melting using mathematical models of the blast furnace process, the following conclusions were made [31,32]:

(a)   The injection of significant (100 kg/t or more) amounts of ore into the furnace leads to a decrease in the degree of direct reduction of iron of materials loaded through the grate. In the blast furnace shaft, due to the withdrawal of a part of iron ore materials equal to the amount of ore blown into the furnace, the ore load decreases, the specific consumption of reducing gas per unit of iron ore materials increases, and the degree of indirect reduction of iron of these materials increases.

(b)   Despite the insignificant residence time (0.01–0.2 s) in the gas flow of the tuyere zone of ore particles blown together with the PUT, the degree of their recovery at a distance of approximately 1 m from the tuyere exceeds 80%. The reduction in iron oxides in the injected ore occurs due to the volatile substances of coal, and the final reduction of iron is due to the solid carbon of coke or semi-coke particles formed from the particles of the injected coal. In all experiments, the injection of ore materials into the furnace autonomously or in a mixture with PUT is accompanied by an increase in total fuel consumption.

(c)   An increase in the consumption of blown iron ore materials up to 100 kg/t or more requires temperature and heat compensation by reducing the humidity of the blast, increasing the oxygen concentration in the blast, and increasing the blast temperature. According to the calculated and experimental data, the joint injection of ore and coal in a ratio of 1:1 does not require any temperature-thermal compensation to maintain the thermal balance of the tuyere zone and does not cause a decrease in the temperature of the gas in the tuyere zone.

(d)   The joint injection of pulverized coal fuel and iron ore is accompanied by a mutual promotional effect of PUT and ore. The presence of coal accelerates the recovery of ore particles in the tuyere zone, and the presence of ore accelerates the combustion process of coal particles and increases the completeness of combustion.

The results of laboratory experiments and mathematical modeling of the injection of iron-containing raw materials were confirmed by studies on industrial blast furnaces [32–35].

With the participation of the Institute of Cast Iron and Steel Technology of the Technical University of the Freiberg Mining Academy (Freiberg, Germany), the companies "Eko-Stahl GmbH" in Azeinhuttenstadt, "STEIN Injection Technology" in Gewelsberg and "Carbofer Verfahrenstechnik" in Meerbusch, a method for recycling oiled scale as part of a mixture of Carbofer consisting of shredding dust and oiled scale was developed rolling shops "Eko-Stahl" (Eisenhüttenstadt, Germany). Industrial tests were carried out in 1996 at blast furnace No. 6 of the Eko-Stahl plant, the mixture was blown through 4 tuyeres with a total consumption of 38 kg/ton of cast iron. According to the participants of the experiments, the experiments showed the fundamental possibility of blowing a mixture of Carbofer into blast furnaces in an amount of up to 150–200 kg/ton of cast iron.

At the company's factory in Sheerness, sludge based on oil-containing scale is mixed with carbon-containing material and dust from electric arc furnaces, and the resulting mixture is blown into an electric arc furnace. The proportion of each component in the mixture is determined by the parameters of the melting operating mode, and the concentrations of each component corresponded to the following limits: oil-containing rolling scale 20–80%; dust of electric arc furnaces 0–60%; carbon 15–25%; lime 0–10% [36].

STEIN Injection Technology (Gefelsberg, Germany) has developed a technology for the disposal of oiled scale by blowing a Sitfer mixture consisting of rolled scale, lime, and coal dust into an electric arc furnace, which contributes to the formation of foamy slag. As a result, energy savings are achieved, melting time and electrode consumption are reduced due to slag foaming technology, and the yield of liquid steel increases [37].

KCC sludge is formed during wet gas purification of converter gases. Slimes are rich (Fe_{com} = 55–67%) or relatively rich in iron (Fe_{com} = 40–55%). During wet gas cleaning, 10–30 kg of sludge is formed per 1 ton of steel being smelted (1–3%) [38]. Consequently, approximately 14–38 million tons of OCS (oxygen converter shop) sludge are formed in the world.

Currently, OCS sludge is characterized by a relatively high content of iron and natural basicity, the main drawback is the high content of non-ferrous metals, especially zinc (more than 1%).

The most widespread use of dehydrated sludge has been found in sintering production as an iron-containing component of sinter. The specific consumption of sludge can reach 200 kg/t of agglomerate. However, a significant disadvantage of this technology is the fact that the content of zinc and lead increases in the resulting agglomerate, which is unacceptable due to the significant influence of these impurities on the masonry of blast furnaces.

The main method of using iron-containing metallurgical slurries (agglomeration, blast furnace, converter, etc.) is their addition to the agglomeration charge. Numerous studies have established that the addition of dust and sludge in the amount of 10–15% (by weight) of the charge (in the absence of harmful substances in them) improves the mechanical strength of the agglomerate, without reducing the productivity of sintering machines [39,40]. In Japan, most factories use iron-containing dust in agglomeration. Some types of dust are processed into unburned pellets on a bundle and loaded into a converter.

Today, in the modern world, billions of tons of various wastes are generated in almost all industries, which, according to their compositions, can act as secondary mineral raw materials [41–59].

Thus, the analysis of technical solutions for the disposal of substandard iron-containing materials at ferrous metallurgy enterprises demonstrates the technological difficulties and disadvantages associated with the disposal of fine composite iron-containing waste, especially oiled scale [60,61]

Well-known technologies for the disposal of oiled scale and sludge either lead to increased wear of equipment and loss of the energy potential of oil or complications of the technology of production and preparation of metallurgical raw materials. The multi-operability and high energy intensity of the processes increase the costs of processing oiled scale [62]. At the same time, from the point of view of resource conservation, the expediency of using fine oiled scale is obvious.

2. Tasks

In order to achieve the best results in the dephosphorization of Lisakov ore and obtaining a metallized product from industrial waste, the following tasks were set:

- Conducting laboratory studies of pyrometallurgical technology of iron ore dephosphorization;
- Study of chemical and granulometric compositions of scale and sludge;
- Investigation of the possibility of obtaining a metalized product from dispersed mixtures prepared from concentrates, composite iron-containing waste (rolling scale, OCS sludge).

3. Methodology

The conducted research can be divided into 4 stages.

The first stage is the determination of chemical and granulometric compositions of scale and sludge.

The second stage: obtaining a semi-product in the form of a sludge from a mixture of converter sludge and rolling scale.

The third stage: obtaining a metalized product for metal smelting.

The fourth stage includes the preparation of metalized pellets—grinding of components to a class of less than 0.1 mm, moistening, and pelletizing to obtain pellets homogeneous in chemical composition and size (fractions of 9–13 mm), and drying and firing of pellets. The finished pellets were subjected to mineralogical analysis using an optical microscope and a micro-X-ray spectral analyzer MS-46 (TSL JSC "AMT", Temirtau, Kazakhstan).

The research was based on the theoretical propositions of solid-phase reduction of metals by carbon.

The method of calculating the amount of carbon required for the reduction of metal oxides is based on determining the amount of charge oxygen to be gasified and the stoichiometric amount of reducing carbon, taking into account the course of solid-phase reactions with both the formation of CO_2 and CO.

4. Results

4.1. Processes for Obtaining a Metallized Product

Determination of the chemical composition of rolling scale and converter sludge (Table 1). The table shows that the rolling scale contains more total iron (73.34%) than the sludge (42.2%) [63].

Table 1. Chemical composition of rolling scale and sludge.

Chemical Composition, %	Rolling Scale	Converter Sludge
Fe_{common}	73.34	42.2
FeO	60.92	43.07
SiO_2	0.595	6.02
Al_2O_3	0.20	0.86
CaO	0.24	27.56
MgO	0.24	4.3
K_2O	Not determined	0.155
Na_2O	-	0.146
TiO_2	-	0.04
MnO	0.40	0.96
P	0.018	0.36
Cr_2O_3	Not determined	0.008
V_2O_5	-	0.028
S_{common}	0.028	0.21
BaO	Not determined	<0.01
Ni	-	0.01
Cu	-	0.021
Zn	-	>0.5 (1.21)
Pb	-	0.068
C_{common}	-	2.13
C_{solid}	-	0.46
Other	-	3.08

The predominant mineral of the sludge is magnetite. Also present are wustite, calcite, hematite, feldspar. The obtained data are in good agreement with the chemical analysis data. The true density of the rolled scale ranged from 4.6 to 4.9 g/cm^3, converter sludge—from 3.5 to 5.0 g/cm^3. Thus, the density of the rolling scale and OCS sludge is comparable.

The analysis of the properties of the specified iron-containing oxide raw materials enables us to conclude that it is advisable to use it in the metallization process. At the same time, the use of a rolling scale is preferable due to the higher content of total iron in it.

The next stage:

The purpose of this part of the experiments is to introduce into production a much less expensive and more efficient method of processing oiled rolled scale of metallurgical production, which will significantly increase the volume of their processing and use them in greater volume in further processing, as well as reduce the environmental burden in

places of concentration of harmful waste of metallurgical production in the form of oiled rolled scale.

The technology of obtaining a semi-product in the form of a precipitate from a mixture of converter sludge and oiled rolling scale was as follows:

(1) Oiled scale and sludge are mixed in a mixer and fed into a vacuum filter (oiled scale is pre-dehydrated at a temperature of 105 °C);

(2) A mixture of the de-oiled scale was used as a filter material (de-oiling of scale is carried out in a drum furnace) and one of the binder components, i.e., the separate components of the charge served as the filter material. Its amount is 25% of the total mass with a proportion of sludge in the mixture of approximately 30%. The filtrate contains no more than 5 mg/L of suspended solids and oils and meets the requirements for process water.

(3) A dehydrated mixture of oiled scale and filter material is fed for firing into a tubular furnace at 650–750 °C.

The scheme for obtaining a semi-product in the form of sludge from a mixture of converter sludge and oiled rolling scale is shown in Figure 1.
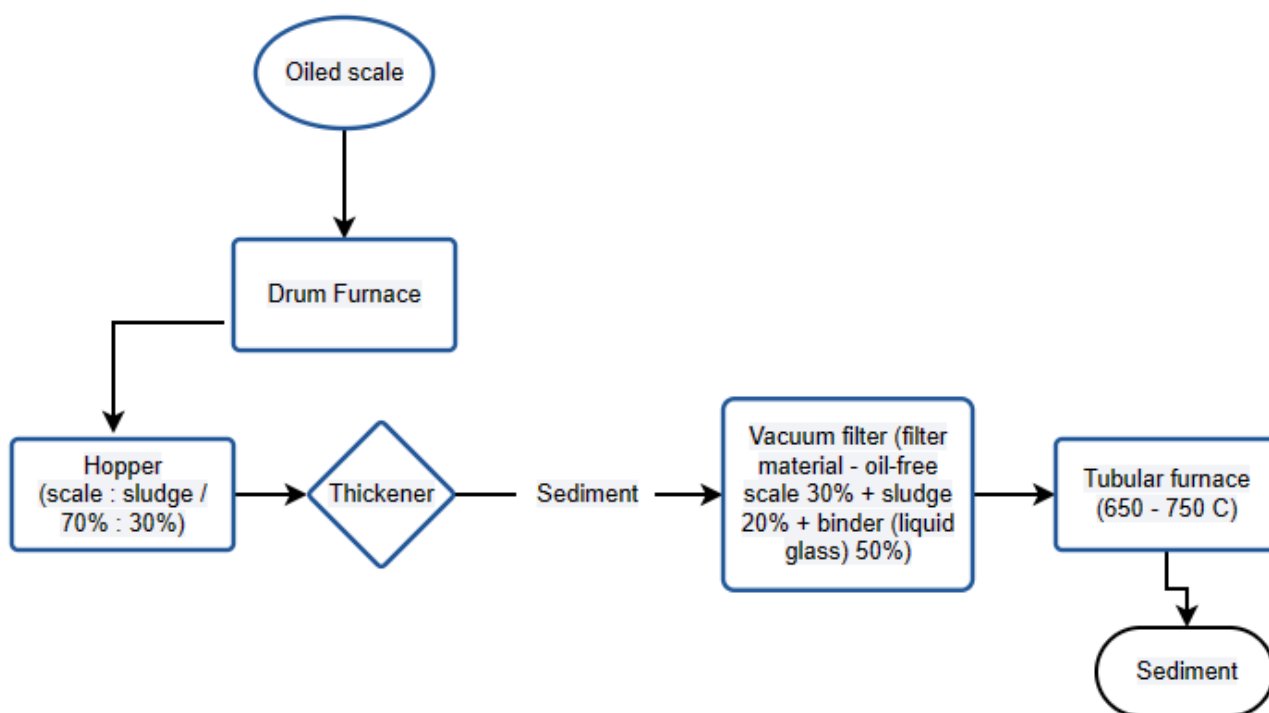

Figure 1. Scheme for obtaining a semi-product in the form of a precipitate from a mixture of converter sludge and oiled rolling scale.

At the end of the process, the resulting precipitate was checked for the remaining oil and moisture content—the oil content was 0.97% by weight, moisture—0.5%.

The next stage of research:

Stages of the tests carried out:

(1) Grinding of LGOK in a ball mill to a class of less than 0.1 mm (sampling of crushed fractions up to 0.1 mm was carried out by sieving through a sieve of the required size);

(2) Obtaining an experimental batch of pellets with a size of 8–16 mm in a pelletizer (concrete mixer) (sinter plant of JSC "AMT", Temirtau, Kazakhstan);

(3) Solid-phase reduction of pellets with carbon under the incendiary furnace of sinter No. 5 (sinter factory of JSC "AMT", Temirtau, Kazakhstan);

(4) Mineralogical analysis using an optical microscope and a microrentgenospectral analyzer MS-46 (TSL JSC "AMT", Temirtau, Kazakhstan), obtained metalized pellets;

(5) Sampling of metalized product for melting;

(6)   Carrying out melting (obtaining metal).

Three types of raw mixtures were studied. The initial compositions of the components contained:

(1)   62.5% LGOK, 25% converter sludge, 12.5% rolling scale, and q = 0.25 kg/kg of charge.
(2)   62.5% LGOK, 18.75% converter sludge, 18.75% rolling scale, and q = 0.26 kg/kg of charge.
(3)   62.5% SSMPPA, 18.75% converter sludge, 18.75% rolling scale, and q = 0.28 kg/kg of charge.

The chemical composition of the materials is shown in Table 2.

Table 2. Chemical composition of materials, %.

Komponents	LGOK	Converter Sludge	Rolling Scale	SSMPPA
Fe_{common}	49.32	46.88	73.33	65.68
Fe_2O_3	70.06	5.44	32.90	62.73
FeO	0.36	55.38	64.67	27.99
Al_2O_3	4.60	0.74	0.23	1.70
SiO_2	11.89	6.41	0.56	4.35
P	0.72	0.65	0.016	0.021
CaO	0.32	22.25	0.55	1.08
MgO	0.46	5.25	0.11	1.16
MnO	0.20	1.46	0.59	0.21
S	0.034	0.154	0.021	0.319

Of the slag-forming oxides in mixtures No. 1, 2, acidic oxides SiO_2 and Al_2O_3 predominate, which causes their low natural basicity (Table 3). Therefore, calculations of the flow rate of the fluxing additive were carried out from the condition of obtaining the basicity of pellets equal to 1.3 units. Lime with CaO content = 92% was used as a fluxing additive.

Table 3. Chemical composition of mixtures, %.

Components	Mixture No. 1	Mixture No. 2	Mixture No. 3
Fe_{com}	51.71	53.36	63.59
Fe_2O_3	49.26	50.98	46.40
FeO	22.15	22.73	40.00
Al_2O_3	3.09	3.06	1.24
SiO_2	9.10	8.74	4.03
P	0.615	0.575	0.138
CaO	5.83	4.48	4.95
MgO	1.61	1.29	1.73
MnO	0.564	0.509	0.516
S	0.062	0.054	0.232
Basicity $((CaO + MgO)/(SiO_2 + Al_2O_3))$. unit	0.610	0.489	1.268

Raw pellets were loaded into a hermetic cell made of metal measuring $0.5 \times 0.5 \times 0.3$ m (width, length, and height, respectively). The cell was placed on the sintering cart (pallet) of the sintering machine, then the pallet was driven under the incendiary furnace of the sintering machine. The furnace temperature during the test period was 1000–1050 °C, at which it was maintained until the gas release stopped, which meant that the iron was completely restored to a metallic state.

Chemical analysis (carried out by atomic emission spectral analysis) of the obtained metalized products showed the following: in the first mixture Fe_{met} = 80.3%, in the second mixture Fe_{met} = 75.8%, in the third mixture Fe_{met} = 70.4%. The degree of metallization of metal products is equal to: for the first mixture—0.98; for the second mixture—0.94; for the third mixture—0.92.

To verify the qualitative and quantitative phase composition, the resulting metalized product was studied in an Empyrean X-ray diffractometer (Karaganda, Kazakhstan)

The Empyrean X-ray diffractometer has metal-ceramic X-ray tubes (long-focus LFF tubes), and the anode material is Cu (copper). It can quickly change the point focus to a linear one by rotating the tube. The type is a high-resolution diffractometer of the Theta-Theta geometry. Fast linear semiconductor detector.

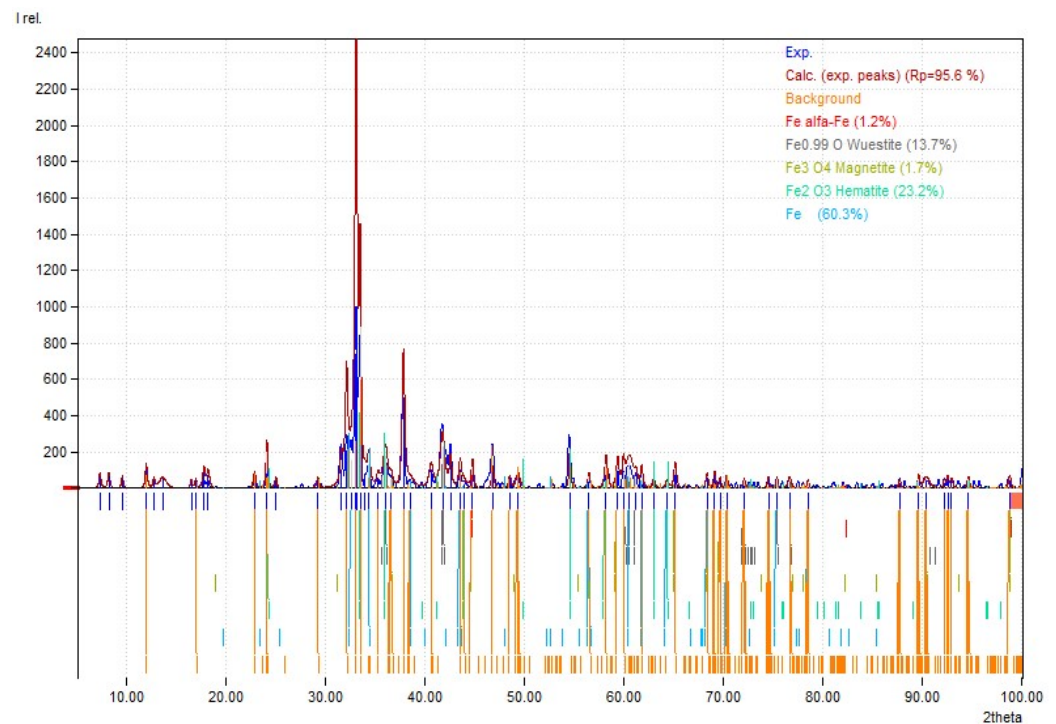The results of the X-ray phase analysis are shown in Figure 2.

Figure 2. Results of the X-ray phase analysis of the resulting metalized product.

Based on the data obtained from the X-ray phase analysis, the following can be noted:

1. The sludge compounds shown on the radiographs were identified by an automatic diffractometer;
2. The main peaks of the phase composition were investigated, which shows that 95.6% of the peak corresponds to iron oxides and elemental iron, as well as alpha iron—the state of iron, that differs from other states in the structure of the crystal lattice, has magnetic properties; the remaining peaks are 4.4% of the peaks correspond to compounds that do not include iron;
3. Quantitative analysis showed that the phase composition of the metalized product consists of α—Fe (alpha iron)—1.2%, wustite—FeO—13.7%, Fe_3O_4—1.7%; Fe_2O_3—23.2%; Fe—elemental iron—60.3%;
4. The presence of elemental iron in large quantities (more than 60%) explains the fact that the resulting metalized product turned out to look like spongy iron.

Samples for melting were taken from the metalized product. Samples of metalized pellets were loaded into glasses and installed in a Tamman melting furnace preheated to 600 °C. To avoid secondary oxidation of metals, the open surface of the glass with the contents was blown with argon. The temperature was increased at a rate of 20 °C/min to 1600 °C, at which the metalized pellets melted and the melt boiling was observed. After 10 min. the glass with the melt was removed from the furnace and cooled to 100 °C. The glass was broken, and the ingot of metal was separated from the slag crust. The resulting metal was analyzed for the content of elements (Table 4).

Table 4. Chemical composition of the resulting metal, %.

No. Mixtures	C	Si	Mn	P	S
1	0.4	0.05	0.2	0.035	0.01
2	0.36	0.04	0.2	0.08	0.02
3	0.38	0.07	0.2	0.09	0.01

The analysis showed that the use of mixture No. 1, where the composition of the charge components contained 62.5% LGOK, 25% converter sludge, 12.5% rolling scale and q = 0.25 kg/kg of the charge, is most preferable both from a technological point of view (the degree of metallization and Fe content are higher by 0.04–0.06 and 4.5–9.9%, respectively) and from the economic side—the cost of LGOK is 2.5-fold lower compared to SSMPPA concentrate, solid fuel economy is 0.1–0.3 t/t of charge.

It has been experimentally established that the reduction with coal (solid carbon) achieves a high degree of metallization of Fe (up to 95.6%).

It was observed that with an increase in the initial iron content in the concentrate, the degree of its reduction by coal increases linearly. This is because an increase in Fe in the concentrate is accompanied by the content of hard-to-recover iron-containing silicates. In addition, the enrichment of the concentrate is accompanied by an increase in its specific surface area.

As a result of the reduction of iron ore concentrates by coal, a metalized product (resembling spongy iron) was obtained with a degree of metallization exceeding 92%. Such studies complement existing studies in this area. The data obtained show that the extraction of iron from composite iron-containing waste seems to be more effective if they are processed to obtain a metalized product, compared with using them as recycled products in sintering production.

4.2. Processes of Dephosphorization of Lisakov Ore

The stages of the tests carried out: preparation of metalized pellets: grinding of components to a class of less than 0.1 mm, moistening, and pelletizing to obtain pellets homogeneous in chemical composition and size (fractions of 9–13 mm), drying and firing of pellets. The finished pellets were subjected to mineralogical analysis using an optical microscope and a micro-X-ray spectral analyzer MS-46 (TSL JSC "AMT", Temirtau, Kazakhstan).

Characteristics of the materials used:

1. Lime. Hardness is 800–1000 kg/m^3. CaO content is 92%
2. Chubarkul coal grade D (long-flame), % (Table 5) Lisakov gravitational-magnetic concentrate, % (Table 6).

Table 5. Chubarkul coal grade D (long-flame), %.

C$_{com}$	C$_{nonvol}$	Ash Content	Volatile	Humidity
72.0	67.0	4.0	25	4.0

Table 6. Lisakov gravitational-magnetic concentrate, %.

Fe$_{com}$	MnO	Zn	Pb	SiO$_2$	Al$_2$O$_3$	CaO	MgO	BaO	S	P	Other
49.32	0.23	0.02	0.012	11.31	4.74	0.32	0.26	0.22	0.021	0.725	11.58

Metalized raw materials were used in the smelting of steel grade "3 ps" on a 300-ton oxygen converter of ArcelorMittal Temirtau JSC (Temirtau, Kazakhstan). Chemical composition of burnt metalized pellets (Table 7) and chemical composition of slag (Table 8) listed below.

Table 7. Chemical composition of burnt metalized pellets.

Basicity	CaO/P$_2$O$_5$	C	S	MnO	P	SiO$_2$	CaO	Al$_2$O$_3$	Fe	Fe$_2$O$_3$
2.0	2.5	8.432	0.088	0.30	0.49	13.81	15.61	3.73	39.11	18.43
2.0	2.5	8.719	0.081	0.23	0.47	11.30	12.58	2.54	42.17	21.91

Table 8. Chemical composition of slag.

FeO	CaO	SiO$_2$	Fe$_2$O$_3$	P$_2$O$_5$	MgO	MnP	S
15–42	40–55	7–13	4–11	1–10	2–5	4–8	0.04–0.20

The tests were carried out in October 2022 in the converter shop of JSC "ArcelorMittal Temirtau" in Temirtau (Kazakhstan).

The process of steel production in an oxygen converter consists of the following main periods: loading of scrap metal, in this case, loading of metalized pellets together with scrap at a ratio of 80:20%, casting of cast iron, oxygen purging, loading of slag-forming materials, draining of steel and slag.

The loading of the converter begins with the filling of steel scrap, simultaneously with the steel scrap with the help of scoops, a metalized product—pellets from LGOK are also fed into the converter. Then, with the help of filling cranes, liquid cast iron is poured, the converter is installed in a vertical position, a tuyere is introduced and the oxygen supply is turned on with a purity of at least 99.5% O$_2$. Simultaneously with the start of purging, the first portion of slag-forming and iron ore (40% of the total amount) is loaded. The rest of the bulk materials are fed to the converter during the purging process in several portions, approximately 5–7 min after the start of purging.

The refining process is significantly influenced by the position of the tuyere (the distance from the end of the tuyere to the surface of the bath) and the pressure of the supplied oxygen. In this smelting process, the height of the tuyere is maintained within 1.0–3.0 m, the oxygen pressure is 1.0–1.4 MPa. Properly organized purging mode ensures good circulation of metal and its mixing with slag. The latter, in turn, contributes to an increase in the oxidation rate of C, Si, Mn, and P contained in cast iron. Slag formation is important in the technology of the oxygen converter process. Slag formation largely determines the course of removal of phosphorus, sulfur, and other impurities, and affects the quality of the steel being smelted, the yield of the suitable, and the quality of the lining. The main purpose of this stage of melting is the rapid formation of slag with the desired properties (basicity, liquid mobility, etc.). The complexity of this task is associated with the high speed of the process (purge duration 14–24 min). The affinity of cast iron elements to oxygen at low temperatures of 1400–1500 °C leads to the oxidation of silicon and manganese, thereby starting the process of slag formation. The formation of slag of the required basicity and the desired properties depends on the rate of dissolution of lime in the slag. The rate of dissolution of lime in the slag is influenced by factors such as the composition of the slag, its oxidation, the conditions for wetting the lime surface with slag, mixing of the bath, temperature conditions, and cast iron composition. At the same time, the oxidation of slag at the beginning of melting is approximately 15–30% depending on the Fe content in the slag, During the period of intense carbon burnout in the middle of the purge, it drops to a minimum and reaches 7–15% (1600–1700 °C). At the end of melting, the higher it is, the lower the carbon content, and at 0.03% carbon reaches 30–40%. In the contact zone of the oxygen jet with cast iron, iron is intensively oxidized, since its concentration is higher than impurities. The resulting iron oxide dissolves in slag and metal, enriching the metal with oxygen. Oxygen dissolved in the metal oxidizes silicon, manganese, and carbon and their content in the metal decreases. In this case, the metal bath is heated by heat released during the oxidation of impurities. Due to the presence of slags released during the dissolution of metalized pellets with a high content of CaO and FeO,

phosphorus is removed from the metal at the beginning of purging the bath with oxygen when its temperature is not yet high. The early formation of the main slag is facilitated by the presence of a primary reaction zone (the contact surface of the oxygen jet with the metal) with a temperature of up to 2500 °C. In this zone, lime is simultaneously exposed to high temperatures and slag with an increased content of iron oxides. The total lime consumption is 5–8% of the melting mass.

A characteristic feature of oxygen converter production is the unevenness of carbon oxidation both in the volume of the bath and during purging. From the first minutes of purging, simultaneously with the oxidation of carbon, the process of dephosphorization begins—the removal of phosphorus. The most intensive removal of phosphorus occurs in the first half of the purge at a relatively low metal temperature, and high content in the slag (FeO); the basicity of the slag and its amount increases rapidly. The oxygen-converter process makes it possible to obtain ≤0.030% P in the finished steel.

When the specified carbon content (0.18%) is reached, the blast is turned off, the tuyere is lifted, the converter is tilted and the metal is poured into the bucket through the fly (to reduce the mixing of metal and slag).

After the experimental melting, the steel of the "3 semi-quiet" brand with the following chemical composition was eventually obtained (Table 9):

Table 9. The chemical composition of the resulting steel.

C	Mn	S	P	Si	Al
0.18	0.42	0.018	0.023	0.12	0.046

This chemical composition of the obtained steel "3 semi-quiet" corresponds to the chemical composition of steel according to GOST 380–94 used in JSC "AMT" Temirtau for rolling pipe steel, which is (Table 10):

Table 10. The chemical composition of the "3 semi-quiet" steel.

C	Mn	S	P	Si	Al
0.14–0.18	0.40–0.55	Up to 0.025	Up to 0.030	0.05–0.15	0.020–0.070

5. Conclusions

As part of the research, the following results were obtained:

- Laboratory studies of pyro- and hydrometallurgical technology (There are hydrometallurgical methods for the treatment of phosphorus from iron ores [4,5]. In one method, soda solutions are used, ore is treated with an alkali solution in another, and with a hydrochloric acid solution in the third. Spanish and French scientists proposed leaching phosphorus with sulfuric acid at room temperature. The disadvantage of this technology is the long (5–25 h) duration of leaching.) of iron ore dephosphorization showed high prospects for its use at the stage of preparation of iron ore for metallurgical processing, which can reliably solve the problem of large-scale production of cast iron and steel at JSC ArcelorMittal Temirtau (Temirtau, Kazakhstan) from high-quality Lisakovsk concentrate with low phosphorus content;

- The process of steel smelting using metalized pellets prepared in advance under laboratory conditions from the Lisakovsky gravitational-magnetic concentrate shows a significant decrease in the concentration of phosphorus in the finished steel, i.e., up to 0.023%, and the supply of scrap mixed with pellets explains the rapid onset of the formation of basic ferrous slag in the converter. Since the phosphorus removal reaction is accompanied by the release of heat, dephosphorization proceeds most intensively in the first half of the purge at a relatively low temperature;

These results are a significant contribution to the development of the process of obtaining more refined steel;

- A method of metallization of iron ore raw materials and waste with carbon has been developed (1400–1600 °C);
- A technology is proposed for the implementation of the metallization process of dispersed raw materials with the possibility of melting hot metalized intermediates;
- Experimentally, a semi-product in the form of a precipitate with an oil content of less than 1% was obtained from an oiled rolling scale for further use as an important component in the production of high-quality steel;
- During metallization, the zinc content will decrease several times, which will enable the use of metalized OCS sludge without restriction due to the negative effect on the lining of blast furnaces;
- Also, the proposed method for obtaining a metalized product makes it possible to use converter sludge to a greater extent. This means that the increased consumption of converter sludge (by 1.33 fold) will have a positive impact on the environment since at the moment the converter sludge is not used and is completely discharged into the ash sludge accumulator. This technology has a further perspective for implementation in production.
- Practically no slag has been melted from carbon-metalized materials.
- Since the main purpose of the experiments was to obtain a metallized product, respectively metallic iron, the extraction of non-ferrous metals, such as zinc and vanadium, was not carried out. But we do not deny that this procedure can be carried out and it will only have a positive impact.

Author Contributions: Conceptualization, M.M. and Y.M.; methodology, D.Y., G.Z. and O.K.; investigation, B.K., B.S. and L.A.; data curation, K.K. and Y.K.; writing—original draft preparation, D.Y. and B.K.; writing—review and editing, M.M., B.K. and Y.K.; visualization, Y.M. and O.K.; project administration, M.M. and O.K. All authors have read and agreed to the published version of the manuscript.

Data Availability Statement: The data used to support the findings of this study are included within this article.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Zharmenov, A.A.; Mukanov, D.M. *Complex Processing of Mineral Raw Materials of Kazakhstan Development of Theory and Practice of Metallurgical Processing of Iron—Alumina Ores*; Dyke Press: Almaty, Kazakhstan, 2003; Volume 4, pp. 158–163.
2. Tazhibayeva, R.M. Optimization of parameters of functioning of mining equipment of iron ore quarries of Kazakhstan. *Bull. KarSU* **2007**, *1*, 101–105.
3. Mirko, V.A.; Kabanov, Y.; Naydenov, V. The current state of development of deposits of brown iron ore in Kazakhstan. *Ind. Kazakhstan* **2002**, *4*, 27–31.
4. Kaskataeva, K.; Kryazheva, T.; Sadchikov, A.; Diyakonov, V. Characteristics of the ores of the Lisakovsky deposit for the purpose of their complex processing. *Proc. Tomsk. Polytech. Univ. Georesour. Eng.* **2021**, *5*, 7–16.
5. Kelamanov, B.; Smailov, S.; Yerzhanov, A.; Apendina, A.; Adilhanov, R.; Kabylkhanov, S. The possibility of involvement in ferroalloy conversion of nickel ores of Kazakhstan. *Metalurgija* **2022**, *61*, 771–773.
6. Kelamanov, B.; Sariev, O.; Akuov, A.; Samuratov, Y.; Sultamuratova, Z.; Orynbassar, R. Study of nickel briquettes by thermographic method. *Metalurgija* **2022**, *61*, 217–220.
7. Samuratov, Y.; Kelamanov, B.; Akuov, A.; Zhumagaliyev, Y.; Akhmetova, M. Smelting standard grades of manganese ferroalloys from agglomerated thermo-magnetic manganese concentrates. *Metalurgija* **2020**, *59*, 85–88.
8. Kelamanov, B.; Samuratov, Y.; Akuov, A.; Abdirashit, A.; Burumbayev, A.; Orynbassar, R. Research possibility of involvement Kazakhstani nickel ore in the metallurgical treatment. *Metalurgija* **2021**, *60*, 313–316.
9. Karelin, V.G. Unit for firing and cooling of Lisakovsky concentrate. In Proceedings of the International Scientific and Practical Conference "Creative Heritage of B.I. Kitaev", Yekaterinburg, Russia, 11–14 February 2009; pp. 166–170.
10. Karelin, V.G.; Zainullin, L.A.; Artov, D.A.; Epishin, A.Y.; Naydenov, V.A. Cooling of annealed fine-grained Lisakovsky concentrate in a rotating drum. *Steel* **2010**, *3*, 6–7.

11. Belikov, V.V.; Ogorodov, V.B.; Yadryshnikov, A.O. Method of Purification of Iron Ore Concentrate from Phosphorus Impurities. Russian Patent 2184158, 23 May 2022.
12. Ionkov, K.; Gaidardzhiev, S.; Bastin, D.; de Araujo, A.C. Extraction of phosphorus from iron ore by acid leaching with the use of alkaline roasting (ARAL). In Proceedings of the Scientific and Practical Conference with International Participation and Elements of the School for Young Scientists "Prospects for the development of metallurgy and mechanical engineering using completed fundamental research and R & D", Yekaterinburg, Russia, 29 October–2 November 2013; pp. 380–388.
13. Singh, M.P.; Naidenov, V.A. Method of Extraction of Waste Rock and Phosphorus from Iron Ore Raw Materials. Kazakh Patent No. 2003/0525.1, 16 April 2003.
14. Levintov, B.L.; Pchelintseva, O.A.; Zeifman, V.M.; Yu, V. Method of Enrichment of Oolitic Brown Limestone Ores. Kazakh Patent No. 2002/0270.1, 5 March 2002.
15. Lunev, V.I.; Usenko, A.I. Method for Obtaining Phosphor-Free Concentrate of Oolitic Iron Ores. Russian Patent 2449031, 17 March 2022.
16. Pchelintseva–Panichkina, O.A.; Levintov, B.L.; Bobir, A.V. Features of structural and phase-chemical transformations in oolitic minerals during firing and leaching of Lisakovsky concentrates. *KIMS* **2005**, *4*, 46–53.
17. Dobrovolsky, I.P.; Ya, I.; Chernyavsky, A.N.; Abyzov, Y.; Kozlov, E. *Processing and Utilization of Industrial Waste of the Chelyabinsk Region*; ChelSU Publishing House: Chelyabinsk, Russia, 2000; p. 256.
18. Gostenin, V.A.; Eliseev, Y.P.; Kovalenkova, E.Y.; Neverovskaya, I.P. Investigation of the possibility of sludge processing in order to obtain iron concentrate. *Steel* **2016**, *4*, 76.
19. Append 1—2020 Integrated Waste Management Report.docx. (saskatoon.ca). Available online: https://www.saskatoon.ca/sites/default/files/documents/transportation-utilities/Waste/2021_integrated_waste_management_rrepor.pdf (accessed on 1 October 2023).
20. Nokhrina, O.I.; Rozhikhina, I.D.; Rybenko, I.A.; Khodosov, I.E. Energy-efficient reduction of iron from its ores. *Steel Transl.* **2016**, *4*, 237–244. [CrossRef]
21. Movchan, V.P.; Vanyukova, N.D.; Kovalev, D.A. Industrial tests of iron ore pellets production technology with the addition of oiled scale of rolling shops. *Min. J.* **2001**, *9*, 68–70.
22. Kekukh, A.V.; Naboka, V.I.; Savyuk, A.N. Investigation of the process of obtaining metallized dipped raw materials of iron-containing waste. Theory and practice of pig iron production. In Proceedings of the International Scientific and Technical Conference, Kryvyi Rih, Ukraine, 24–27 May 2004; KGGMK "Krivorozhstal": Kryvyj Rih, Ukraine, 2004; pp. 584–587.
23. Kekukh, A.V.; Linetsky, B.M.; Kripak, S.N. Technology of utilization of oiled scale in the production of coke. Theory and practice of cast iron production. In Proceedings of the International Scientific and Technical Conference, Kryvyi Rih, Ukraine, 24–27 May 2004; KGGMK "Krivorozhstal": Kryvyj Rih, Ukraine, 2004; pp. 587–590.
24. Shermet, V.A.; Kekukh, A.V.; Kripak, S.N. Processing of oiled scale of rolling production by the method of low-temperature cracking. Theory and practice of pig iron production. In Proceedings of the International Scientific and Technical Conference, Kryvyi Rih, Ukraine, 24–27 May 2004; KGGMK "Krivorozhstal": Kryvyj Rih, Ukraine, 2004; pp. 590–591.
25. Kurunov, I.F.; Savchuk, N.A. The state and prospects of the homeless metallurgy of iron. *M. Chermetinf.* **2002**, *1*, 198.
26. Munnix, R.; Borlee, J.; Steyls, D. Comet-new coal-based process for the production of DRI. *MTR Int.* **1997**, *2*, 50–62.
27. Borlee, J. The Comet process-DRI from fines and coal. *Steel Times* **1996**, 399.
28. Frieden, R.; Hansmann, T.; Monai, J. *PRINUS, a New Process for the Recycling of Be-Products and the Preproduction of Iron Ore*; 4 European Coke and Ironmaking Congress: France, Paris, 2000; Volume 2, pp. 504–509.
29. Hansmann, T.; Frieden, R.; Monai, J. New process for recycling steelmaking wastes and pre-reduction of iron. *Millenn. Steel Lead. Rev. Adv. Process Technol. World-Wide* **2001**, 105–110.
30. Borlee, J.; Steyls, D.; Colinet, R. COMET: Un procede utilisant du charbon hour produire une eponge de fer qualite a partir de minerai de fer. *Rev. Metall.* **1999**, *3*, 332–339.
31. Kurunov, I.F. Prospects for the use of uncut iron-containing materials in a blast furnace. *Metallurg* **2003**, *5*, 37–44.
32. Kurunov, I.F. Investigation of the effectiveness of desiliconization of cast iron when blowing iron ore materials into a blast furnace. *Metallurg* **2003**, *6*, 40–44.
33. Gudenau, G.V.; Wippermann, S.; Moskovchuk, V.P. Studies on the pluvannu of iron ore fines in a blast furnace. *Steel* **1996**, *2*, 9–11.
34. Yamagata, C. Development of ultra combined blasting for blast furnace. *CAMP ISIJ* **1991**, *4*, 1020–1023.
35. Yamagata, C. Actual test results on simultaneous injection of pulverized coal and fine ore into tuyere at Wakayama No. 3 BF. *CAMP ISIJ* **1991**, *4*, 144.
36. Cartwright, D.; Clayton, G. Recycling oily millscale and dust by injection into the EAF. *Steel Times Int.* **2000**, *24*, 42–43.
37. Danilov, E.V. Economical method of utilization of metallurgical and rolling rocks in chipboard using Sitfer technology. *Metallurgist* **2003**, *5*, 49–50.
38. Panishev, N.V.; Bigeev, V.A.; Chernyaev, A.A.; Panteleev, A.V. Processing of metal-grained waste of metallurgical production with the production of granular cast iron and zinc extraction. *Theory Technol. Metall. Prod.* **2014**, *2*, 22–26.
39. Burovoy, I.A.; Usachev, A.B. Method of Direct Production of Steel and Iron-Containing Materials. Russian Patent RU2346056C2, 10 February 2009.
40. Tleugabulov, S.M.; Kiyekbayev, E.; Koishina, G.M.; Aldangarov, E.M. Direct reduction of metals leads to high production technology. *Steel* **2010**, *2*, 4–8.

41. Nadirov, R.K.; Nadirov, K.S.; Bimbetova, G.Z.; Nadirova, Z.K. Synthesis and cytotoxic activity of new flavopiridol analogs. *Chem. Nat. Compd.* **2016**, *52*, 499–500. [CrossRef]

42. Kolesnikov, A.S.; Sergeeva, I.V.; Botabaev, N.E.; Al'zhanova, A.Z.; Ashirbaev, K.A. Chemical and phase transitions in oxidized manganese ore in the presence of carbon. *Steel Transl.* **2017**, *47*, 605–609. [CrossRef]

43. Nadirov, K.S.; Zhantasov, M.K.; Sakybayev, B.A. The study of the gossypol resin impact on adhesive properties of the intermediate layer of the pipeline three-layer rust protection coating. *Inter. J. Adhes. Adhesiv.* **2017**, *78*, 195–199. [CrossRef]

44. Zhangabay, N.; Suleimenov, U.; Utelbayeva, A.; Kolesnikov, A.; Baibolov, K.; Imanaliyev, K.; Moldagaliyev, A.; Karshyga, G.; Duissenbekov, B.; Fediuk, R.; et al. Analysis of a Stress-Strain State of a Cylindrical Tank Wall Vertical Field Joint Zone. *Buildings* **2022**, *12*, 1445. [CrossRef]

45. Kolesnikova, O.; Vasilyeva, N.; Kolesnikov, A.; Zolkin, A. Optimization of raw mix using technogenic waste to produce cement clinker. *MIAB Min. Inf. Anal. Bull.* **2022**, *60*, 103–115. [CrossRef]

46. Zharmenov, A.; Yefremova, S.; Satbaev, B.; Shalabaev, N.; Satbaev, S.; Yermishin, S.; Kablanbekov, A. Production of Refractory Materials Using a Renewable Source of Silicon Dioxide. *Minerals* **2022**, *12*, 1010. [CrossRef]

47. Filin, A.E.; Ovchinnikova, T.I.; Zinovieva, O.M.; Merkulova, A.M. Advance of pulsating ventilation in mining. *Gorn. Zhurnal.* **2020**, *3*, 67–71. [CrossRef]

48. Satbaev, B.; Yefremova, S.; Zharmenov, A.; Kablanbekov, A.; Yermishin, S.; Shalabaev, N.; Satbaev, A.; Khen, V. Rice Husk Research: From Environmental Pollutant to a Promising Source of Organo-Mineral Raw Materials. *Materials* **2021**, *14*, 4119. [CrossRef] [PubMed]

49. Petrov, V.V.; Protsenko, A.E.; Sapozhnik, K.R. Solid-cabide tool waste recycling technology. *Constr. Mater. Prod.* **2022**, *5*, 27–34. [CrossRef]

50. Urakaev, F.K.; Khan, N.V.; Shalabaev, Z.S.; Tatykaev, B.B.; Nadirov, R.K.; Burkitbaev, M.M. Synthesis and photocatalytic properties of silver chloride/silver composite colloidal particles. *Colloid J.* **2020**, *82*, 76–80. [CrossRef]

51. Marenov, B.T.; Nadirov, K.S.; Zhantasov, M.K.; Nadirov, R.K. Ethylene-vinyl acetate copolymer/crude gossypol compositions as pour point depressants for waxy oil. *Int. J. Chem. Eng.* **2020**, *2020*, 4195382. [CrossRef]

52. Zakrevskaya, L.V.; Gavrilenko, A.A.; Kapush, I.R.; Lyubin, P.A. Creating ground concrete and strengthening substrates using mining waste. *Constr. Mater. Prod.* **2022**, *5*, 35–44. [CrossRef]

53. Michaeli, E.; Solár, V.; Maxin, M.; Vilček, J.; Boltižiar, M. The Nature of the Technosols on the Waste from Nickel Production. *Sustainability* **2021**, *13*, 406. [CrossRef]

54. Lezhnev, S.; Panin, E.; Volokitina, I. Research of combined process rolling-pressing influence on the microstructure and mechanical properties of aluminium. *Adv. Mater. Res.* **2013**, *814*, 68–75. [CrossRef]

55. Zhu, D.; Jiang, Y.; Pan, J.; Yang, C. Study of Mineralogy and Metallurgical Properties of Lump Ores. *Metals* **2022**, *12*, 1805. [CrossRef]

56. Naizabekov, A.; Volokitina, I.; Volokitin, A.; Panin, E. Structure and Mechanical Properties of Steel in the Process "Pressing–Drawing". *J. Mater. Eng. Perform.* **2019**, *28*, 1762–1771. [CrossRef]

57. Ljana, M.; Paananen, T.; Mattila, O.; Kondrakov, M.; Fabritius, T. Effect of Iron Ore Pellet Size on Metallurgical Properties. *Metals* **2022**, *12*, 302. [CrossRef]

58. Hiraga, R.; Gomes, O.F.M.; Neumann, R. Maghemite in Brazilian Iron Ores: Quantification of the Magnetite-Maghemite Isomorphic Series by X-ray Diffraction and the Rietveld Method, and Confirmation by Independent Methods. *Minerals* **2021**, *11*, 346. [CrossRef]

59. Mróz, J.; Konstanciak, A.; Warzecha, M.; Więcek, M.; Hutny, A.M. Research on Reduction of Selected Iron-Bearing Waste Materials. *Materials* **2021**, *14*, 1914. [CrossRef] [PubMed]

60. Mukhametkhan, M.; Mukhametkhan, Y.; Tleugabulov, S.; Zhabalova, G.; Shevko, V. Thermodynamic interaction of concentrate, sludge and mill scale from carbon. *Metalurgija* **2021**, *60*, 289–291.

61. Mukhametkhan, Y.; Mukhametkhan, M.; Tleugabulov, S.; Zhabalova, G. Complete thermodynamic analysis of the interaction of iron phosphate ($FePO_4$) with hydrogen (H_2) and carbon monoxide (CO). *Metalurgija* **2021**, *60*, 306–308.

62. Kurunov, I.F.; Tikhonov, D.N.; Erokhin, S.F. Resource-ecological technology of utilization of oiled scale. In Proceedings of the Collection of Theses of the Scientific and Practical Conference Energy Resource Saving at Metallurgical and Mining Enterprises (New Solutions), St. Petersburg, Russia, 19–22 January 2004; pp. 16–17.

63. Mukhametkhan, M.; Mukhametkhan, Y.; Zhabalova, G.; Kamkina, L. Investigation of physico-chemical characteristics of iron-containing technogenic raw materials in the conditions of JSC "AMT". *Metalurgija* **2023**, *62*, 129–131.