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THE REDUCTION SMELTING
OF METAL-CONTAINING INDUSTRIAL WASTES

Abstract. Metal containing scrape accumulation is not only issue of the ecological safety of regions, but is a new paradigm in development of the black metallurgy (direct production of iron) obtaining the energy and resources conservation policy.

The purpose of the work: use of metal-containing and carbon-containing industrial waste – converter sludge and coal sludge of the JSC "ArcelorMittal Temirtau" metallurgical enterprise.

The process structuring chain consists of: 1) ore-coal mixture conditioning from converter and coal slimes; 2) production of ore-coal pellets from the fine ore-coal mixture; 3) metallization of ore-coal pellets; 4) reduction smelting of metallized pellets and production of natural-alloyed steel.

The solid carbon was used as a reducing agent, while preparing the ore-coal mixture we adhere to the principle of complete reduction of the net extracted iron and manganese metals. Therefore, the stoichiometric consumption of prepared coal sludge per unit of iron ore concentrate was determined according to the developed procedure, taking into account the sequentially phase transformation of oxides. As a result of performed calculations, the coal feed rate per unit of concentrate in the amount of 0,265 kg/kg was obtained. The ore-coal mixture consisted of the sum of prepared converter and coal sludges.

On the basis of metal- and carbon-containing sludge of JSC "ArcelorMittal Temirtau" the ore pelletized pellets with stoichiometric carbon content areobtained. Sequential processing, drying, metallization and reduction smelting made it possible to obtain metal ingots corresponding to high-quality steel in composition in the final stage.

Key words: metal-containing waste, converter sludge, coal sludge, metallization, pellets, steel, carbon, phosphorus, reduction, smelting, crystallization.

The conventional technology of metallurgical production of cast iron and steel is based on the two-stage complex "Blast furnace-Converter". At the initial stage of the complex, conventionally, agglomerate oxide materials are used as raw materials in the form of sinter and pellets in predetermined weight ratios to the mass of coke. The mass fraction of coke in the charge provides the thermal balance of the reduction smelting process as a source of hot reducing gases (HRG) used to heat the charge column and to reduce iron, and also to melt the ore portion of the charge.

In addition, the coke layer plays an important role as a nozzle in which counterflow filtration of HRG and melts is realized, as well as a source of direct reduction of iron and hard-to-reduce metals by solid carbon. As can be seen, under the conditions of implementation of the reduction-smelting process in the blast furnace there is a stable excess of coke and the melted metal product is cast iron.

In view of high performance of blast furnaces, the worldwide mass production of structural materials is based on the oxygen converter processing of pig iron via oxidation smelting into steel. The problem of oxidation smelting of cast iron in the oxygen converter is metal decarburisation. However, during oxygen

lancing of the iron melt, not only the oxidation of the carbon of the cast iron occurs, but also the oxidation of a significant part of iron and the complete oxidation of the valuable alloying metals with formation of metal oxides, which are transported into the converter slag. In converter smelting, not only the formation of metal-containing slags occurs, but a significant mass of sludges with concentration of metals many times higher than in slag. They are also accumulated in dumps.

Metal-containing wastes accumulation is a problem nowadays not only for the environmental security of the regions, but also as a secondary source of raw materials for the production of metal [1].

Pursuance of the most low-cost use of these wastes is associated with their return, if possible, according to the current scheme of the metallurgical cycle, in particular, to the agglomeration process. However, the possibility of introducing dispersed metal-containing waste into the sintering charge is limited and the mass of the incandescent metal-containing waste is expanding every year.

Analyzing new theoretical propositions [2] and the organization of the processes of mini production of iron and steel [3-5], one may come to the conclusion that the last word of science is related not only to the existing principle of the preparation of the agglomerated oxide raw material and its reducing melting, but a new principle of preparation of disperse metal-containing raw materials and its reduction-smelting processing.

Such an approach opens the prospect of not only the full use of current and accumulated waste, but also the direct production of high-quality steels and alloys from them.

The principle of agglomerated oxide raw material (agglomerate, pellets) preparation is based mainly on the use of HRG as a reducing agent, which requires high gas permeability of the burden layer. The very organization of the reduction processes in countercurrent of the agglomerated charge column and HRG from the position of the process kinetics has a number of significant drawbacks. The commonly advertised adsorption-catalytic mechanism (ACM) [6] is not a determining factor in the realization of metal reduction. On the contact surface between the agglomerated raw material and HRG, the metal reduction mechanism is associated with a topochemical mass transfer regime [7], by the successive phase transformation of the oxides into a metallic state from the surface to the center of the pieces. Such a sequence of the process is limited by the slowest contact-diffusion mechanism.

In the processes of metallization of dispersed metal-containing waste, HRG cannot be used as a reducing agent. The most effective reducing agent is solid carbon, which does not require gas permeability of the layer, while at the same time provides a high rate of reaction depending on the value of the RSC coefficient (reaction-contact surface). The value of the RSC in the 1,0 mm thick dispersible waste layers reaches up to 20,000 m^2/kg, and below 1,0 mm can reach up to 30,000 m^2/kg.

Conditions for the realization of direct reduction of metals is, first of all, the uniform distribution of a carbon-containing reagent of a similar reaction in a layer of dispersed oxide waste. Based on this principle of charge preparation, experimental studies were carried out.

Experimental procedure. In the experimental studies, metal-containing and carbon-containing industrial wastes - converter sludge and coal sludge chemical compositions of which are presented in table 1 from the JSC "ArcelorMittal Temirtau" metallurgical enterprise were used.

It can be seen from the composition of the initial slimes that the content of the basic CaO oxide is almost 4-times higher than the concentration of acid oxides ($SiO_2+Al_2O_3$) in fluxes. Hence it can be seen that phosphorus and sulfur with concentration of 0,5 and 0,2% are in the form of chemical compounds of $Ca_3(PO_4)_2$ and CaS, respectively. Coal sludge also contains rather high concentration of slag-forming oxides - SiO_2и Al_2O_3.

Table 1 – Chemical composition of initial components

Name of components	Chemical composition, %									
	Fe_{com}	FeO	MnO	SiO_2	Al_2O_3	CaO	MgO	S	P	C
Converter sludge	60,3	12,5	1,75	2,54	3,25	22,0	2,32	0,20	0,50	2,65
Coal sludge	–	–	–	18,2	7,65	2,32	0,72	0,18	0,05	52,3

Therefore, the initial sludge was pretreated to remove a part of the slag-forming gangue. Both sludges were enriched: converter sludge - by magnetic separation, and coal sludge - by gravity concentration.

In the dry coal sludge the specific weight of slag-forming oxide particles (SiO_2, Al_2O_3, CaO, MgO) is, on average, five times greater than the specific mass of solid carbon particles. Within respective limits, their hovering velocities vary, i.e. particles removal rate. These variations were used for separation in the wind tube, which was charged with dry coal sludge and the layer was purged with air at a rate of 5,0-6,0 m/s, which corresponds to fine carbon particles hovering velocity. Smaller and lighter particles are blown through a special vent and enters the second container - dust collector. The trapped dust mainly contained carbon particles.

The compositions of enriched converter and coal sludges are presented in table 2.

Table 2 – Chemical composition of processed converter and coal sludges

Name of components	Chemical composition, %									
	Fe_{com}	FeO	MnO	SiO_2	Al_2O_3	CaO	Mg	S	P	C
Converter sludge	71,25	14,75	1,93	1,51	1,92	12,75	1,33	0,02	0,12	2,95
Coal sludge	–	–	–	6,86	2,87	0,87	0,27	0,06	0,02	65,74

As can be seen from the results of the analysis presented in table 2, rather qualitative components - iron ore concentrate with high iron content and a carbonaceous reagent with a carbon content of 65% were obtained from the initial converter and coal sludges. Only phosphorus content in the concentrate is much higher than the allowable rate. However, it should be stipulated that high concentration of basic CaO oxide in converter sludge is associated with the technology of dephosphorization of pig iron in an oxygen converter in which oxidized phosphorus P_2O_5 is bound by calcium oxide according to the following reactions:

$$2[P]+2,5O_2 = P_2O_5 \tag{1}$$

$$P_2O_5 + 3\,CaO = Ca_3(PO_4)_2 \tag{2}$$

As can be seen, phosphorus dissolved in the cast iron, oxidized in P_2O_5 by reaction (1), binds firmly to calcium phosphate by reaction (2). Considering the high chemical strength of $Ca_3(PO_4)_2$, in the organization of subsequent reduction and smelting processes, it is advisable to regulate the temperature-heat regime of phosphorus reduction. Based on this formulation of tasks, the following sequence of organization of the process was adopted.

1. Preparation of ore-coal mixture from converter and coal sludges.
2. Obtaining ore-coal pellets from the fine ore-coal mixture.
3. Metallization of ore-coal pellets.
4. Reduction smelting of metallized pellets and obtaining nature-alloyed steel.

Since solid carbon is used as the reducing agent, when preparing the ore, the coal mixture is based on the principle of complete reduction of the useful extractable metals of iron and manganese. Therefore, the stoichiometric consumption of the prepared coal sludge per unit of iron ore concentrate was determined according to the developed procedure, taking into account the successive phase transformation of oxides [8]. As a result of the performed calculations, the consumption of coal cuttings per unit of concentrate in the amount of 0,265 kg/kg was obtained. The ore-coal mixture consisted of the amount of prepared converter and coal sludges in the amount of 1+0,265 = 1,265 kg. The resulting dispersed ore-coal mixture was thoroughly mixed, then ore-carbon pellets were obtained from the pellet granulator. An aqueous solution of nitrocellulose varnish was used as a binder. Mixing of converter and coal sludges inevitably leads to a change in the chemical composition of the mixture, in which the mass fraction of ore and coal parts was determined from the ratio $\gamma_p=1,0:1,265=0,79$ and $\gamma_y= 0,265 : 1,265 = 0,21$. Based on these mass ratios, the average chemical composition of the mixture was determined, which is presented in Table 3.

Obtained crude pellets with fraction of 8,0-20,0 mm after drying at 400^0C have acquired sufficient strength and have been prepared for metallization.

Since the pellets contain an increased concentration of phosphorus and a stoichiometric amount of carbon in choosing the temperature regime, not only the direct reduction of metals by carbon was taken into account, but also the possibility of limiting the transition of phosphorus to the metal. Here the favorable effect is due to the fact that phosphorus is completely in the compounds of calcium phosphate, from which it begins to recover only at temperatures above 1200 °C. Therefore, the metallization process was limited to heating to 1000-1100 °C.

The dried pellets with a mass of 200 g were placed in a sealed cell made of a quartz tube with a diameter Ø40 mm and introduced into the tubular furnace SUOL-044 12-M2, preheated to 550 °C, then heated at a rate of 10 °C/min. At 650 °C, the beginning of expelling of the gas - the reaction products of CO and CO_2 was recorded. When temperature reached 1100-1120 °C, a time delay of 25-30 minutes was observed until the gas expelling ceased, which meant the completion of the direct reduction of metals.

The chemical composition of ore-coal and metallized pellets is presented in table 3.

Table 3 – Chemical composition of ore-coal and metallized pellets

Name of pellets	Chemical composition, %										
	Fe_{com}	Fe_{met}	FeO	Mn	SiO_2	Al_2O_3	CaO	MgO	S	P	C
Ore-coal	56,29	–	11,65	1,18	2,63	2,12	10,25	1,107	0,036	0,10	16,13
Metallized	86,6	84,0	3,34	1,81	4,05	3,26	15,77	1,70	0,04	0,154	2,15

Samples of metallized materials together with the cell were removed from the furnace, cooled and further reloaded into a refractory crucible and installed in a "Tamman" melting furnace. The furnace was heated at a rate of 15-20 °C/min. In order to avoid secondary oxidation of the metallized pellets, the surface of the crucible was blown with neutral gas - argon. When the temperature reached 1600 °C, the pellets were completely transferred to the melt, which was drained into a refractory baking sheet.

The yield of metal was 68,0 g. from the initial 200 g. of ore-coal pelletized pellets. Analysis of metals obtained from two runs is provided in table 4.

Table 4 – Chemical composition of samples of molten metal

Metal samples	Chemical composition, %				
	[Mn]	[C]	[Si]	[S]	[P]
Test № 1	1,20	0,57	0,15	0,02	0,028
Test № 2	1,25	0,62	0,12	0,025	0,030

As can be seen from the results of the analysis, melted samples of metal are nature-alloyed steels. The content of contaminants - sulfur and phosphorus meets the technical requirements of high-quality steel.

Conclusion. On the basis of metal-containing and carbon-containing sludge of JSC "ArcelorMittal Temirtau", ore pelletized pellets with stoichiometric carbon content are obtained. Sequential processing of drying, metallization and reduction smelting made it possible to obtain in the final stage metal ingots, which in composition correspond to high-quality steel.

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ҚҰРАМЫНДА МЕТАЛЛ БАР ӨНЕРКӘСІПТІК ҚАЛДЫҚТАРДЫ РЕДУКЦИЯЛАП БАЛҚЫТУ

Аннотация. Құрамында металл бар қалдықтардың жинақталуы бүгінгі таңда тек өңірлердің экологиялық қауіпсіздігі мәселесі ғана емес, сондай-ақ энергия мен ресурстарды үнемдеу саясатын есепке ала отырып, қара металлургия саласы дамуының жаңа парадигмасына (тікелей темір өндірісі) байланысты болуы керек.

Жұмыстың мақсаты: «АрселорМиттал Теміртау» АҚ металлургиялық комбинатының құрамында металл бар және көміртегі бар қалдықтар – конвертерлік шлам мен көмірді байыту шламдарын пайдалану.

Процесті ұйымдастыру кезектілігі мынадай: 1) конвертер және көмір шламдарынан кенді көмірлі қоспаны дайындау; 2) ұсақ кен көмірлі қоспадан кен көмірлі окатыштер алу; 3) кен көмірлі окатыштерді металлизациялау; 4) металданған окатыштерді редукциялап-балқыту және легірленген болат алу.

Тотықсыздандырғыш реагент ретінде қатты көміртегі қабылданған-дықтан, кен көмірлі қоспаны дайындау кезінде темір мен марганец металдарынан алынған пайдалыларды толық тотықсыздандыру принципіне сүйенеміз. Сондықтан оксидтердің реттік-фазалық түрленуін ескерумен әзірленген әдістеме бойынша темір рудалы концентрат бірлігіне дайындалған көмір шламының стехиометриялық шығыны анықталды. Есептеулерді орындау нәтижесінде 0,265 кг/кг мөлшерінде концентрат бірлігіне кететін көмір шламының мөлшері алынды. Көмір кенді қоспа конвертерлік және көмір шламдарының сомасынан құралды.

«АрселорМиттал Теміртау» АҚ жағдайындағы құрамында металл бар және көміртегі бар шламдарының негізінде көміртегінің стехиометрлік құрамымен көмірлі окатыштер дайындау ұйымдастырылды. Оларды ретімен өңдеу, кептіру, металдандыру және редукциялап-балқыту соңында сапалы болаттың құрамына сәйкес келетін металл құймасын алуға мүмкіншілік береді.

Түйін сөздер: құрамындаметалл бар қалдықтар, конвертерлік шлам, көмір шламы, металдау, окатыш, болат, көміртегі, фосфор, редукциялау, балқыту, кристалдану.

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ВОССТАНОВИТЕЛЬНАЯ ПЛАВКА МЕТАЛЛОСОДЕРЖАЩИХ ПРОМЫШЛЕННЫХ ОТХОДОВ

Аннотация. Накопление металлсодержащих отходов сегодня является проблемой не только экологической безопасности регионов, но и должно быть связано с новой парадигмой развития черной металлургии (прямое получение железа) с учетом политики энерго- и ресурсосбережения технологий.

Цель работы: использовать металлосодержащие и углеродсодержащие промышленные отходы металлургического комбината АО «АрселорМиттал Темиртау» - конвертерный шлам и шлам углеобогащения.

Последовательность организации процесса состоит из: 1) подготовка рудоугольной смеси из конвертерного и угольного шламов; 2) получение рудоугольных окатышей из мелкий рудо угольной смеси; 3) металлизация рудоугольных окатышей; 4) восстановительная плавка металлизованных окатышей и получение природолегированной стали.

В качестве восстановительного реагента принят твердый углерод, при подготовке рудо угольной смеси исходим из принципа полного восстановления полезных извлекаемых металлов железа и марганца. Поэтому был определен стехиометрический расход подготовленного угольного шлама на единицу железорудного

концентрата по разработанной методике с учетом последовательно-фазового превращения оксидов. В результате выполненных расчетов получен расход угольного шлама на единицу концентрата в количестве 0,265 кг/кг. Рудоугольная смесь состояла из суммы подготовленных конвертерных и угольных шламов.

На базе металлсодержащих и углеродсодержащих шламов АО «АрселорМиттал Темиртау» организована подготовка рудоугольных окатышей со стехиометрическим содержанием углерода. Последовательная обработка сушка, металлизация и восстановительная плавка позволила получить на завершающей стадии слитки металла, которые по составу соответствуют качественной стали.

Ключевые слова: металлсодержащий отход, конвертерный шлам, угольный шлам, металлизация, окатыш, сталь, углерод, фосфор, восстановление, плавка, кристаллизация.

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