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Analysis of Different Types of Carbonaceous Reductants and Methods of Slag and Sludge Recovery at Converter Production

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Abstract. *Recycling of metal-containing wastes with an iron content of more than 15%, such as slag and sludge from the gas cleaning of converter production, can be used to recover the metal. In order to study the reducing properties of coal sludge, coke breeze (coke), Shubarkol coal, a series of experimental melting of coal sludge briquettes with different contents of the listed carbon-containing materials was carried out. Sludge-coal briquettes were made from converter slag and sludge using hydrated lime as a binder. To determine the necessary parameters for the reduction of the iron-containing element, chemical and technical analyzes were carried out for ash content, moisture content and volatile matter. The choice of the optimal component composition of briquetted mixtures has established that the proportion of the reducing agent in the briquette should not exceed 20...25%, in order to avoid excess carbon, which binds into solid carbide compounds. The share of the reducing agent in the briquette was 15...18%. Chemical analysis of the resulting alloy and slag component pointed out the expediency of using Shubarkol coal as a carbonaceous reducing agent with high reactivity and electrical resistivity.*

Keywords: *converter slag, converter slime, coal slime, Shubarkol coal, coke dust, briquette, smelting.*

Introduction

Solid-phase carbon metallization technology makes it possible to process finely dispersed materials without subjecting them to additional processing – pelletizing. The solution to this problem is based on the use of solid carbon as the main reducing agent. Solid carbon or carbon-containing solid reducing agent occupies a volume 935 times smaller than an equal amount of carbon in the gas reducing agent. The solid carbon takes 2.5 times as much oxygen from the iron oxides as the carbon in the gaseous reducing agent (CO_2). There is a difference in temperature control between gaseous and solid (carbon) reduction which has to be compensated by external sources [1].

There are many substances known to perform reductive functions, the main ones being coal, coke, fuel oil and charcoal. Secondary resources include coal dust – waste from various industries such as thermal power plants, coking plants, coal flotation waste, i.e., in general, materials that need to be recycled in terms of ecology and the possibility of getting economic benefits from their recycling.

During metal converting, depending on metal charge composition, unit design and melting technology, fine dust of up to 12÷25 kg/t of steel is generated, the degree of exhaust gas cleaning from dust is more than 80%, the degree of recycling is 72% [2, 3].

Recycling of sludge into the production cycle simultaneously solves a number of important tasks: provides enterprises with iron-containing raw materials, solves environmental problems of fine waste recycling, contributes to saving of natural raw materials and reducing the cost of produced steel. In this regard, the application of efficient recycling technologies is one of the urgent tasks of modern metallurgy.

Main part

For the recycling of iron-containing dispersed waste, alternative processes to agglomeration could be pelletizing or briquetting.

Briquetting provides wide opportunities for utilization of fine wastes, it is also promising in terms of metallized product, as reductants can be introduced into the composition of the briquetted charge. The advantage of briquettes as compared to reduced pellets is the lower value of open porosity, as a result of which briquettes are not subject to active secondary oxidation in the atmospheric air [4].

Briquetting is a less costly method of waste disposal compared to sintering or the production of fired pellets. Processes of briquetting of fine waste are more technologically advanced than other methods of pelletizing, because the quality of briquettes is least dependent on the granulometric composition and humidity of the initial material, and their size, shape and chemical composition can be adjusted in a wide range by selecting the size and shape of the matrix cells, the choice of binders and introduction of various additives [4].

The advantages of briquetting are that this method makes it possible to obtain conditioned products with adjustable dimensions and technological properties from waste of different chemical composition and properties, to increase the density of bulk materials, to prevent the freezing and caking of fine waste in hoppers and dosing equipment.

Analysis of research findings

The aim of the study is to determine the optimum component composition providing iron-carbon briquettes with favorable chemical and technological properties, minimum cost and compliance with mechanical strength requirements. In particular, the briquettes must withstand thermal shock when piling them into the furnace, have high soften ability and shrinkage, minimizing secondary oxidation of iron by the furnace atmosphere.

The composition of the starting iron-containing materials is shown in Table 1.

A very valuable iron-containing technogenic raw material is converter sludge, in particular converter sludge of JSC «ArcelorMittal Temirtau», which contains up to 48% of iron [6, 7]. The main part of sludge is represented by Fe_2O_3.

From the converter slag (Fe content up to 25%) and slime were made slime-coal briquettes using hydrated lime as a binder. Slag briquettes of size 55×100 mm were made at different ratios of slag and slag from the total iron content in the briquette mixture. The ratios of converter slag to converter slag were 80:5; 75:5; 70:5; 67:5; 62:5, the amount of injected binder lime varied from 5 to 15%, using three different reductants from 10 to 18% (Table 1).

In selecting a reductant for recycling metal-containing industrial waste, experimental studies have been carried out using different reductants such as Shubarkol coal, coal sludge and coke.

The reducing power of carbon materials is determined by the volatile matter and ash content, the porous structure, and the specific surface area [8, 9].

Chemical and technical analyses for ash content, moisture content and volatile matter yield were carried out to determine the necessary parameters for iron recovery (Tables 2 and 3).

The analysis has shown that any of the above types is suitable for use as a carbon-containing component of the briquette mixture. It is more appropriate to use coal dusts from different metallurgical process stages, in terms of saving energy and material resources.

A series of experimental melts were carried out to investigate the reducing properties of slime-coal briquettes pelletised with different carbon-containing materials. In the process of electric melting of slime-coal briquettes based on a mixture of converter slime and converter slag, sulphur combustion was observed. Sulphur in coal is a harmful impurity. When using coal in metallurgy, sulphur is transferred to metal, deteriorating its quality [9, 10].

After smelting, the metal part and the slag part were weighed and the results were summarised. The results for recoverability are presented in Table 4.

Samples of metallized materials weighing 350, 450, 500 g of the three items presented in Table 4 were melted in a Tamman furnace. The melting resulted in alloy ingots whose yields and chemical composition are presented in Tables 5 and 6.

Table 1 – Composition of initial iron-bearing materials

№	Materials, in %					
	K_S	K_{Sl}	Lime	U_{shub}	U_{slam}	Coke
1	62	5	15	18	-	-
2	70	5	10	15	-	-
3	64	5	5	16	-	-
4	62	5	15	-	18	-
5	70	5	10	-	15	-
6	64	5	5	-	16	-
7	62	5	15	-	-	18
8	70	5	10	-	-	15
9	64	5	5	-	-	16

Table 2 – Chemical composition of feedstock and materials for the production of iron-carbon briquettes

Material from	Chemical composition, %				
	SiO_2	CaO	MgO	FeO	Fe_2O_3
Converter sludge	3,33	12,92	0,34	88,15	1,87
Converter slag	7,48	44,68	4,55	23,36	11,82
Shubarkol coal	64,79	9,25	-	-	5,24
Coke	39,73	1,97	0,29	-	3,87
Coal sludge	9,03	0,92	0,23	0,15	1,06
Hydrated lime	1,26	65,69	1,14	-	0,98
Liquid glass (dry)	51,71	0,41	-	-	-

Table 3 – Technical analysis of carbon materials

Material name	Zola, A^d	Volatile, V^d	Moisture, W^a	Carbon content, C^{daf}	Sulphur content
Shubarkol coal	2,8	-	-	82	0,4
Coke	13,6	7,8	4,8	85	0,6
Coal sludge	15,8	22,9	1,4	80	0,4

Table 4 – Smelting briquettes based on a mixture of BOF slag and slag

No. of experiences	Weight briquette, g	Metal, %	Slag, %	Gas, %
1	350	33,03	60,95	6,02
2	450	25,03	67,5	7,47
3	500	26,23	65,28	8,49
4	350	19,95	75,02	5,03
5	450	17,7	73,04	9,26
6	500	18,74	75,31	5,95
7	350	28,01	63,94	8,05
8	450	22,85	68,07	9,08
9	500	24,29	70,47	5,24

Table 5 – Chemical analysis of metal

Sample number	C	Si	Mn	P	S
1	0,15	0,8	0,2	0,05	0,065
2	2,73	2,45	0,78	0,38	0,0018
3	3,71	3,29	1,08	0,5	0,002
4	0,022	0,009	0,02	0,05	0,035
5	0,53	0,85	0,23	0,06	0,052
6	0,46	0,15	0,62	0,028	0,03
7	2,55	2,39	1,03	0,3	0,002
8	2,94	3,64	0,98	0,48	0,0025
9	5,45	3,00	1,16	0,54	0,003

Conclusions

The following conclusions can be drawn from the chemical analysis of the slag phase:

1. The high Fe_{total} content in the slag phase indicates incomplete reduction of iron oxides, when coal dust is used.

Table 6 – Chemical analysis of the slag component

№	Fe_{total}	CaO	MgO	SiO_2	Al_2O_3	P_2O_5	SO_3	MnO	ZnO
1	24,9	18,0	22,9	5,71	3,03	1,22	1,25	0,69	0,16
2	27,7	14,4	14,3	5,61	2,48	1,56	1,12	0,88	0,16
3	30,6	44,7	12,5	9,1	3,26	0,27	0,61	1,38	0,15
4	57,7	14,4	14,3	5,61	2,48	1,56	1,12	0,88	0,16
5	44,9	18,0	22,9	5,71	3,03	1,22	1,25	0,69	0,16
6	36,3	40,8	6,81	6,77	4,43	0,92	2,92	0,49	0,008
7	26,0	55,0	3,16	5,82	4,15	0,70	3,88	0,57	0,04
8	34,7	20,87	2,19	5,33	1,87	0,25	0,61	1,38	0,15
9	41,5	58,1	8,58	8,57	4,42	0,51	1,05	1,09	0,06

2. When coke and Shubarkol coal are used as reducing agents, a more complete reduction of iron oxides is observed.

3. It is more appropriate to use Shubarkol coal. The advantage of Shubarkol coal as a carbon reducing agent is its high CO reactivity$_2$ at 1000°C – 5,1 cm^3/(g-s) against 0,47 cm^3/(g-s) of coke and a very high resistivity – more than 1,9×106 Ohm-cm against 3,9 Ohm-cm of coke.

Coke and coal sludge introduce ash and harmful impurities into the charge, thereby reducing the quality of the smelted metal.

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Көміртекті тотықсыздандырғыштардың әр түрлі түрлерін және конвертерлық өндіріс шлактары мен шламдарын кесектеу әдістерін талдау

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***Аңдатпа.** Құрамында 15%-дан астам темір бар металл қалдықтарын қайта өңдеу, мысалы, конвертерлік шлактар мен конвертерлік газды тазарту шламдары металды алу үшін пайдаланылуы мүмкін. Көмір шламының, кокстің ұсақтарының (коксша), Шұбаркөл көмірінің тотықсыздандыру қасиеттерін зерттеу мақсатында құрамында көміртек болатын материалдардың мөлшері әртүрлі шлам көмірлі брикеттердің эксперименттік балқыту сериясы жүргізілді. Конвертерлік шлактар мен шламдардан гидратталған әкті байланыстырушы ретінде қолдана отырып, шламкөмірлі брикеттер жасалды. Құрамында темір бар элементті тотықсыздандырудың қажетті параметрлерін анықтау үшін күлге, ылғалға және ұшпа заттардың шығуына химиялық және техникалық талдау жүргізілді. Брикеттелетін қоспалардың оңтайлы компоненттік құрамын таңдау брикеттегі тотықсыздандырғыштың үлесі қатты карбидті қосылыстарға қосылатын көміртектің артық болуын болдырмау үшін 20...25%-дан аспауы керек деп тапты. Брикеттегі тотықсыздандырғыштың үлесі 15...18% құрады. Алынған қорытпа мен шлак компонентіне химиялық талдау Шұбаркөл көмірін жоғары реактивтілігі мен нақты электр кедергісі бар көміртекті тотықсыздандырғыш ретінде пайдаланудың орындылығын көрсетті.*

***Кілт сөздер:** конвертерлік қож, конвертер шламы, көмір шламы,шұбаркөл көмірі, кокс шаңы, брикет, тотықсыздану, балқыту.*

Анализ различных видов углеродистых восстановителей и методов окускования шлака и шлама конвертерного производства

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***Аннотация.** Рециклинг металлосодержащих отходов с содержанием железа более 15%, таких как шлаки и шламы газоочистки конвертерного производства может быть использован для извлечения металла. С целью исследования восстановительных свойств угольного шлама, коксовой мелочи (коксика), Шубаркольского угля проведена серия экспериментальных плавок шламоугольных брикетов с различным содержанием перечисленных углесодержащих материалов. Из конвертерных шлака и шлама изготавливали шламоугольные брикеты с применением в качестве связующего звена гидратированной извести. Для определения необходимых параметров восстановления железосодержащего элемента проведен химический и технический анализы на зольность, влажность и выход летучих веществ. Выбор оптимального компонентного состава брикетируемых смесей установил, что доля восстановителя в брикете не должна превышать 20…25%, во избежание избытка углерода, который связывается в твердые карбидные соединения. Доля восстановителя в брикете составляла 15…18%. Химический анализ полученных сплава и шлаковой составляющей указал на целесообразность использования шубаркольского угля как углеродистого восстановителя с высокими реакционной способностью и удельным электросопротивлением.*

***Ключевые слова:** конвертерный шлак, конвертерный шлам, угольный шлам, шубаркольский уголь, коксовая пыль, брикет, плавка.*

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