CARBON REDUCTANT FOR SILICON METAL PRODUCTION

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ABSTRACT

Development of domestic production of silicon metal in Kazakhstan is seriously complicated by scarcity of forests covering only 3% of territory. In spite of significant reserves of high-purity quartz, comparably cheap energy and favorable market situation, the traditional charcoal-based scheme of silicon production is unsuitable for Kazakhstan. A search for alternative form of carbon as a substitute for charcoal in silicon process is crucial for successful implementation of silicon projects in Kazakhstan.

The paper describes a new type of reductant for silicon metal smelting, its physical properties regarding specifics of silicon process and lab-scale tests in 0,2 MVA furnace made separately with two kinds of quartz of Kazakhstan deposits.

Industrial tests of Recsil in 25 MVA submerged arc furnace of Silicium Kazakhstan silicon plant showed positive prospects for the new type of reductant.

KEYWORDS: *Metal silicon, SAF, new reductant, microstructure, charcoal.*

INTRODUCTION

Finding alternative types of reductants and development of industrial smelting technology of silicon with a partial or total substitution for the charcoal a crucial task for Kazakhstan, where shortage of forest resources prevents domestic production of charcoal - a traditional reductant for smelting of pure grades of metal silicon.

It is indisputable that charcoal is one of the best carbon reducing agents, meeting the basic requirements of silicon electrosmelting technology. The low content of impurities and highly developed finely porous structure ensures significant chemical activity and electrical resistance and, as a consequence, intensive flow of recovery reactions during the smelting.

However, along with above benefits, use of charcoal as major reductant has several disadvantages, both economic (such as high cost and scarcity) and technical – low content of fixed carbon and low mechanical strength. In addition, production of charcoal is linked to deforestation that sometimes inflicts irreparable environmental damage.

A new type of carbon reductant – “Carbonizate Recsil” created in Kazakhstan can partially or completely replace charcoal in the smelting of high-quality technical silicon. By various quality parameters which play important role in silicon production, Recsil is similar to charcoal, but in some aspects it is superior.

An attractive feature of new reductant is a fact that for the first time in the history of silicon production an effective reductant is made of available mineral – coal, instead of phytogenous material.

Creation of Recsil and its commercialization opens positive prospects for development of domestic silicon production and may soon become a significant event because it does not cause deforestation leading to disruption of the Earth's ecosystem.

Recsil production is ecologically pure and is accompanied by formation of a considerable amount of heat which can be used to produce electric energy required for silicon production.

CHARACTERIZATION OF RECSIL

Recsil is produced by high speed thermooxidative carbonization of Shubarkol coalfield (open-pit mining) with confirmed reserves of coal reaching 2.0 billion tons (Kazakhstan). Finished product is a granular silver-black lump material. Lump size is in the range of 5-40 mm, bulk density is 0,32-0,36 t/m^3, structural strength up to 70%, residual volatile level 0.1-3.5%. By the level of admixtures Recsil is close to charcoal, because about half of its ash is silica while total ash content is 2.5 - 5.5%. Comparative data on characteristics of Recsil and traditional reductants used for silicon smelting are shown in table 1.

Table 1: Quality parameters of different types of carbon reductants

Parameter	Petroleum coke	Charcoal	Recsil
Technical composition, %			
A^d	0,22	1,96	3,35
V^{daf}	8,20	17,43	2,63
W^p	8,70	12,02	1,64
S^d_t	0,58	0,002	0,34
Structural strength, %	64,3	39,0	70,0
Reactivity at 1273 K, ml/g·s	0,42	7,2	4,2
Electrical resistance, Ohm·cm at 700 K	20,0	155,0	5,0
1900 K	0,87	1,32	3,6
Ash chemistry, %			
SiO_2	46,30	2,16	51,85
Al_2O_3	6,97	3,48	17,94
CaO+MgO	18,52	50,68	3,56
Fe_2O_3	14,20	2,42	7,32
P_2O_5	0,24	3,45	0,38
K_2O+Na_2O	10,13	12,89	2,71
TiO_2	0,26	-	0,81
Average pore size, μm	315,0	15,12	14,57
Fixed C, %	82,30	70,49	92,04

Figure 1 shows microstructure of commercial Recsil produced by LLC "ARMAK 1" (Kazakhstan). Fractographic Recsil microstructure images were obtained be means of SEM using «JEOL» JSM-5910 microscope.

It is seen that Recsil has a finely developed porous structure, with inner surface of pores, reaching 150-300 m^2/g. Recsil structure is formed by pores of different shapes, such as transitional, communicating, closed, separated by various geometries interporous walls, as a whole forming a highly permeable material available for silicon-containing gases. At the same time orientation and distribution of pores in the volume is random and uniform, the structure of Recsil is isotropic, homogeneous and finely porous.

The structure of charcoal (figure 2), on the contrary, is characterized by pronounced anisotropy. Thus, it is evident that only a share of inner surface is available for interaction with SiO gas, about 13-15% by some researchers [1]. Compared by this parameter the charcoal is inferior to Recsil, thus making the latter a reasonable alternative and indicating the feasibility of partial or full substitution of Recsil for charcoal with maintaining performance characteristics of silicon process.

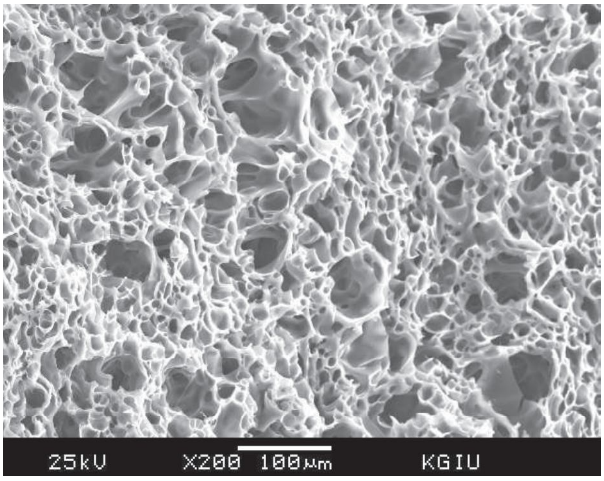
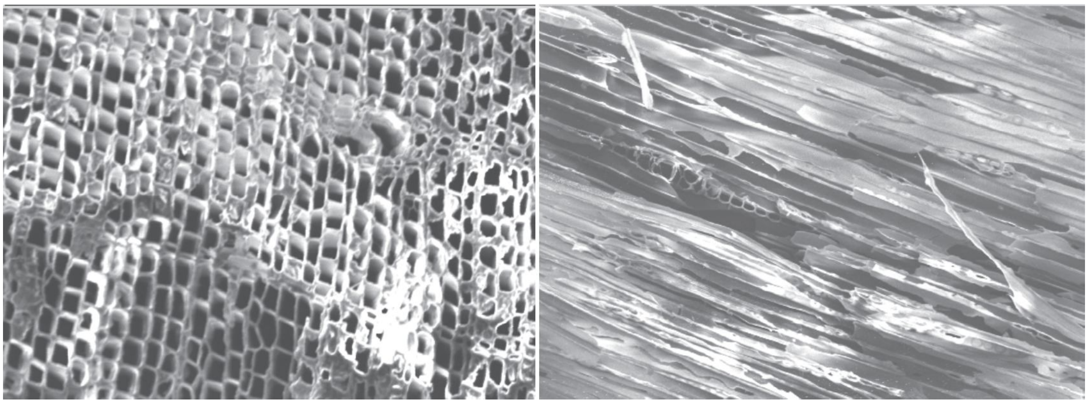


Figure 1: Microstructure of Recsil surface

Table 2: Parameters of Recsil microstructure, µm

Pore size		Averaged pore size	Average thickness of interporous walls
Lengthwise	Crosswise		
18,12	11,01	14,57	4,22



a) b)

a) cross-section × 200; b) longitudinal section × 200

Figure 2: Microstructure of charcoal

Petroleum coke (figure 3) is a widespread carbon composite used in production of silicon to cut the overall cost of reductant, reduce its ash content and improve quality of silicon.

Petroleum coke is a product of thermal treatment of heavy residues of oil. It is seen that petroleum coke microstructure is characterized by individual large-size pores located at far greater interporous distances. The porous structure as such is not observed which is probably the main reason for its low reactivity.

An important property of carbon reductant for carbothermal silicon production is specific electric resistance. Practical experience of SAF silicon production shows that electrical regime of silicon smelting, distribution of Joule heat between charge and electric arc, energy density in reaction zone, and, consequently, the electrical efficiency of furnace, are determined by electric resistivity of carbonaceous component of charge mixture in the temperature range 100-1900 K [2].

Specific electric resistance of charge mixtures containing Recsil and charcoal was studied using resistance furnace.

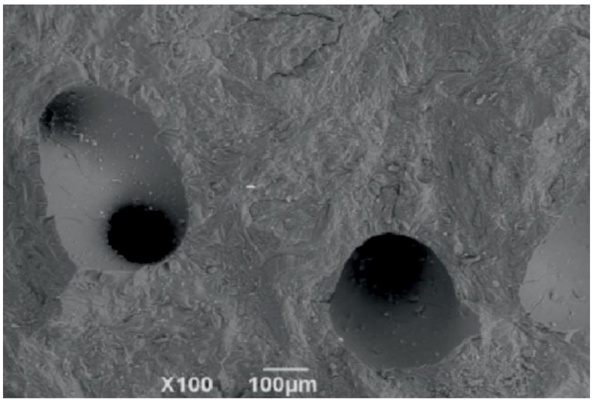


Figure 3: Microstructure of petroleum coke, × 100

A higher electric resistance of charge containing Recsil, in comparison to charcoal and wood chips charge is also a notable feature of Recsil, figure 4.

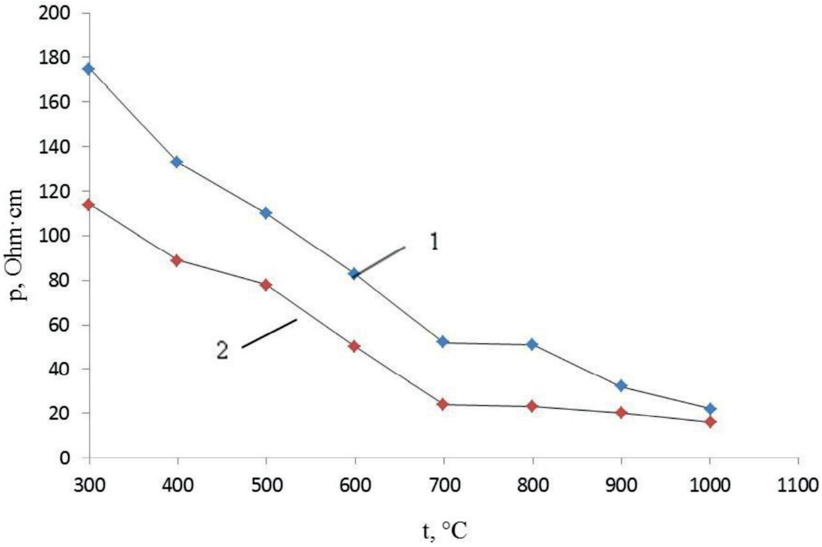


Figure 4: Temperature dependence of electric resistivity of charge with Recsil (1) and charcoal (2)

The data presented in the table 1 and figure 4 show that in high-temperature zone Recsil has significant advantage over compared carbon reductants in terms of specific electric resistance and the higher the temperature the more pronounced is the difference.

LAB-SCALE SMELTING

Below are the results of Recsil laboratory tests performed in a pilot 200 kVA SAF. Smelting of silicon was made by continuous process with periodic charge loading and tapping in every 2 hours.

Smelting campaign included 4 periods: one control period and three experimental ones.

In all stages, the raw materials for silicon smelting was Aktas quartz (Central Kazakhstan) with grain size 10-25 mm.

A distinctive feature of the quartz is high purity. Average chemical composition of quartz is as follows, %: SiO_2 – 99,8; Al_2O_3 – 0,17; CaO – 0,02.

The objective of lab-scale smelting was assessment of Recsil efficiency as a reductant for silicon process. Performance characteristics of smelting process with Recsil were compared to those of traditional charge composition including charcoal, wood chips and raw coal of Shubarkol coalfield. Charge composition of smelting periods and process parameters are represented in the table 3.

Table 3: Technical characteristics of silicon smelting _ with quartz deposits "Aktas"

Parameter	Control period (1)	Experimental period 2	Experimental period 3	Experimental period 4
Composition of bed charge, (sample charge with 10 kg of quartz), kg: Quartz	10,0	10,0	10,0	10,0
Charcoal	3,8	-	-	-
Recsil	-	3,0	4,1	5,1
Shubarkol coal	3,3	4,0	1,6	-
Wood chips	3,3	-	-	-
Specific furnace capacity, kg/h	2,7	2,9	3,3	2,5
Si extraction degree, %	77,0	81,0	91,0	76,0
Average Si content, %	96,5	97,2	97,8	96,4
Specific energy consumption*, MWt·h/t	15,53	16,34	14,95	16,84

* - it should be noted that energy consumption in lab furnace is significantly higher than in industrial SAFs due to smaller size and greater heat loss

In the control period the charge composition was identical to that of "Silicium Kazakhstan" 25 MVA furnace. During the first period about 300 kg of quartz was processed and total 116 kg of metal was obtained. According to State Standard GOST 2469-69, produced metal corresponded to grade Kr3 (above 96% Si). Overall Si extraction degree was 77,0%.

In the period 2 the charcoal and wood chips were replaced by Recsil and raw coal with Recsil/coal ratio by fixed carbon 60/40%. Substitution was followed by increase of furnace specific capacity from 2.7 to 2,9 kg/h with higher extraction degree of silicon (81,0%).

Highest rate of silicon recovery was achieved in the third period of the pilot campaign, when Recsil share was increased to 80% by fixed carbon.

In general, the process flow with charcoal replaced by Recsil was more smooth and stable with deeper immersion of electrode and firmer amperage. Charge was heated evenly, creating favorable conditions for intensive development of recovery reactions.

Furnace productivity increased to 3.3 kg/h, Si extraction degree reached 91.0%, specific energy consumption was reduced by 3,7% compared to control period.

Switching to operation on pure Recsil without addition of raw coal or wood chips caused degradation of performance characteristics – instable amperage, slow performance, agglomeration of charge on top of furnace and, consequently, led to lower Si extraction, decreased capacity and higher energy consumption. Disorder of smelting regime resulted in lower quality of metal.

Second campaign on silicon smelting was carried out with quartz of Sarykul deposit (Southern Kazakhstan) with the following characteristics: grain size 10-25 mm, composition,%: SiO_2 – 99,3; Al_2O_3 – 0,06; Fe_2O_3 – 0,16; CaO – 0,08.

Charcoal and Recsil were used as basic reductants and additions of wood chips were used to "loosen" the charge bed.

Tested charge compositions and the results of second pilot campaign are represented in the table 4.

Table 4: Performance characteristics of silicon smelting from Sarykul quartz

Parameter	Period			
	Control	**Transitional**	**Experimental**	**Control ***
Voltage level, V	36	36	36	36
Period duration, h	40	20	34	18
Consumed materials, kg				
Quartz	492,0	130,0	250,0	128,0
Charcoal	264,3	29,2	0,0	48,3
Recsil	0,0	39,1	135,7	0,0
wood chips	66,0	39,0	48,0	38,5
Metal obtained**, kg	101,3	43,5	107,6	52,3
Average tapping weight, kg	4,05	4,35	6,73	6,54
Specific capacity, kg/h	2,11	2,18	3,16	2,91
Average Si content, %	96,62	96,41	97,24	96,06
Si extraction degree, %	62,77	69,83	90,58	86,95

* - Control Period was repeated for confirmation.

** - metal containing above 94.0% Si.

A traditional charge composition was tested in the control period with charcoal and wood chips used as reductants. Work of the furnace in this period was characterized by lowest productivity and extraction of silicon. Tapping weight in the control period averaged 4.05 kg.

In transitional period charcoal was being gradually substituted to Recsil, first reaching charcoal/Recsil ratio 33 to 67% with further increase of Recsil share to 100% and complete withdrawal of charcoal.

Replacement of charcoal to Recsil was accompanied by a number of phenomena indicating intensification of recovery processes . In the experimental period the performance characteristics of smelting process reached maximum for whole campaign.

Analysis of smelting results shows that the work with 100% Recsil with addition of wood chips was accompanied by extension of melting space leading to a substantial increase in average tapping weight to 6.73 kg against 4.05 kg in the control period. As a result, productivity was noticeably increased and reached 3.16 kg/h which is about 30% higher than in control period.

Silicon extraction degree reached 90.58% and metal purity was highest for whole campaign exceeding 99,5% on the number of occasions.

Distinctive features of furnace performance during the experimental period were as follows: deeper immersion of electrode, more stable amperage, smooth gas evolution over the whole area of the furnace top.

Subsequent furnace switching to basic charge composition (repeated control period) was accompanied by deterioration of nearly all parameters of smelting process. Moreover, it was observed that performance characteristics were declining throughout all repeated control period. All attempts to improve the parameters of the process failed.

Comparison of results of control and experimental test periods indicate that smelting of metal silicon from Sarykul quartz is more advantageous with Recsil than with charcoal.

CONCLUSION

Thus, the results of two silicon smelting campaigns carried out in a pilot 200 kVA SAF show that Recsil is a reasonable alternative to charcoal as it provides better furnace performance and higher process characteristics and quality of metal. Analysis of furnace performance with various charge components shows that addition of wood chips or high-volatile charcoal for loosening of charge is preferable to working on pure Recsil.

Considerable advantage of Recsil is its substantially lower price which is more than two times lower than that of charcoal.

Even at equal price Recsil has economic advantages in terms of higher content of fixed carbon: over 95% against 77-90% of fixed carbon in charcoal.

By now the technology of silicon smelting with Recsil is successfully implemented at "Silicium Kazakhstan" metal silicon smelter in 25 MVA furnaces.

Over 5 thousand tons of Recsil were processed during the commercial tests at "Silicium Kazakhstan" plant proving the possibility of complete substitution of Recsil for charcoal.

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