

## COST ADVANTAGE AND QUALITY ADVANTAGES IN THE LARGE SCALE MANUFACTURING OF METALLURGICAL SILICON (MG-SI)

A. Betekbaev, B. Mukashev, K. Ounadjela, D. Skakov, V. Timoshenko, A. Pavlov

*This report presents the results of using petroleum coke and slag purification in large-scale pilot production of various process parameters. The purpose of this paper demonstrate the ability to remove a substantial amount of B and P on a large scale, using appropriate processes, the slag processing, while maintaining the silicon melt in a liquid form. The results obtained with high removal efficiency Al, Ca, B and P of MG-Si - 99%, 99%, 64% and 68% respectively.*

*Keywords: metallurgical silicon, slag refining, slag, oxides, UMG silicon.*

### 1 INTRODUCTION

Refining of metallurgical-grade silicon (MG-Si) to a higher performance Metallurgical Silicon is a very important scientific topic in silicon research nowadays due to its potential as a cheaper and efficient alternative route for the fabrication of low-cost solar-grade silicon (SoG-Si) feedstock that lead to the manufacturing of solar PV modules. This type of MG-Si material is also used in the pharmaceutical industry where a lower amount of dopants makes the material more suitable to inject in the fabrication process. The main innovation in the KazSilicon process concerns the three processes that relates to the smelting furnace technology and Slag purification of the MG-Si to reduce the amount of dopants in the Silicon material. This is not a single process that makes the difference but the combination of both technologies.

For the smelting furnace, a new design and technology were implemented at KazSilicon for the utilisation of the Petroleum coke rather than the use of charcoal. The main advantage of using Petroleum coke is reduction in cost compared to the use of Charcoal but also in the reduction in the amount of dopants present into the source of Carbon. This leads to an increase in the quality of the MG silicon. These points have been demonstrated with MG silicon production at KazSilicon, resulting in a significant amount of electricity consumption reduction, production efficiency improvement and the quality of the final product.

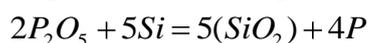
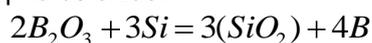
For slagging, the main purpose is the refining of MG silicon with a reduced amount of dopants into the material more specifically the reduction of metallic elements, as well as B and P.

Most of the published work on refining MG-Si are done at a lab scale (Si in grams to few kg), this paper presents the refining results with

petroleum coke and slagging refining in our large scale pilot production with different operational parameters.

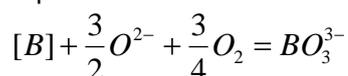
### 2 BACKGROUND OF SLAG REFINING

Slag refining is one of most economical method to purify MG-Si. The method involves oxidation of the impurity element, which dissolve into the slag phase. Due to their high affinity for oxygen, elements such as Al, Ba, Ca and Mg can be removed from silicon by oxidation alone as shown in Figure 1 [1]. However, oxides of B and P are more stable than SiO<sub>2</sub>, resulting in the limited B and P removal by oxidation, as Si reduce B and P from Boron oxide and Phosphorus oxide.

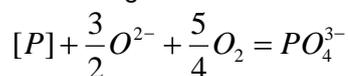


To remove B and P to a low level by oxidation, a significant amount of Si will be lost as SiO<sub>2</sub> in slag, which is making the process not cost effective and difficult to manufacture. A proper slag can form a slag complex with B and P, more stable than SiO<sub>2</sub>. The purpose of this paper is to demonstrate on large scale manufacturing the ability to remove significant amount of B and P using the proper slag processes while keeping the Silicon in a liquid form.

The overall reaction of boron removal is then expressed as



At higher P<sub>o<sub>2</sub></sub>, phosphorus enters the slag via the following reaction.



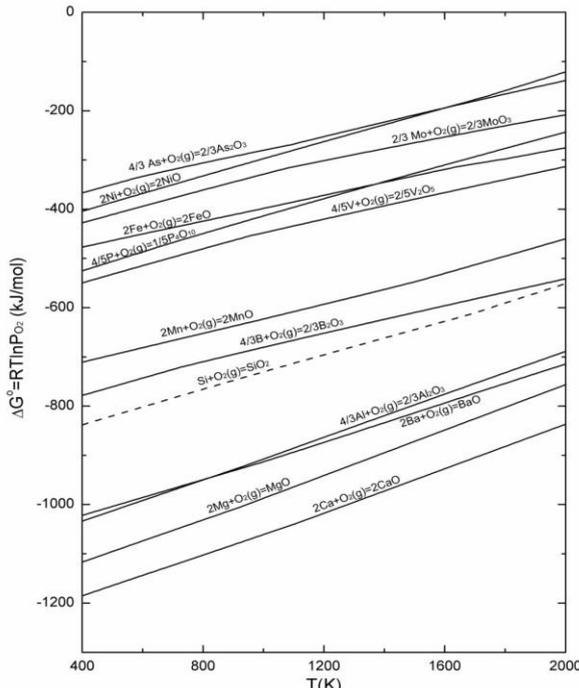
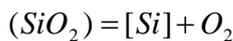
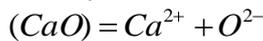


Figure 1. Ellingham diagram for oxides[1]

Oxygen ions ( $O^{2-}$ ) in the above reactions are provided to the slag by the dissociation of basic oxides such as  $CaO$ ,  $BaO$  or  $Na_2O$ , while under equilibrium conditions the  $p_{O_2}$  is established through following as the dominant metal/oxide phases.



The extent of impurity removal by slagging is often quantified by the distribution coefficient ( $L_M$ ), the ratio of concentration in wt%, of impurity M in the slag phase (M) to that in the metal phase [M] as shown in the following equation.

$$L_M = \frac{(M)}{[M]}$$

The higher the value of  $L_M$ , the more effective of the slag system to remove B and P. Several simple slag systems, generally based on  $CaO-SiO_2$ , have been proposed for the treatment of MG-Si, including:  $CaO-CaF_2$ , [2]  $CaO-SiO_2$  and  $CaO-SiO_2-CaF_2$ , [3-5]  $CaO-SiO_2-BaO$  and  $CaO-SiO_2-MgO$ , [6]  $CaO-SiO_2-Al_2O_3$ , [7]  $CaO-SiO_2-Al_2O_3-MgO$  and  $BaO-SiO_2-Al_2O_3$ , [8] and  $Na_2CO_3-SiO_2$ . [9]. A summary of their experimental results are presented in the figure 2.

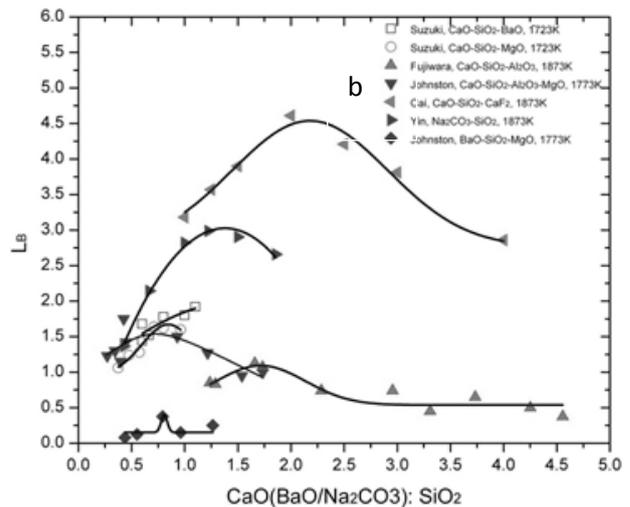
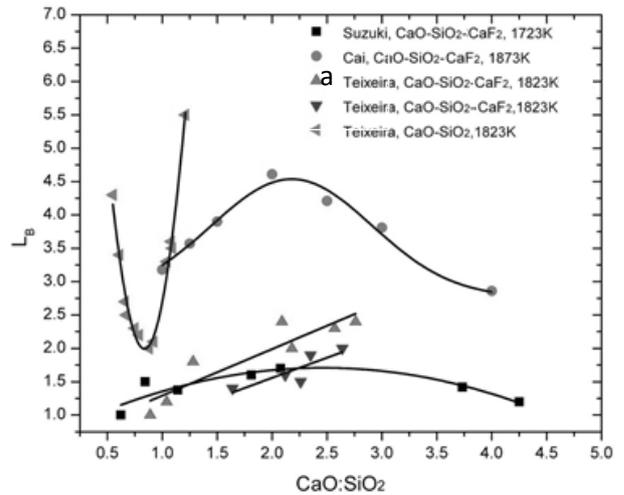


Figure 2 B distribution vs a function of slag composition expressed in a)  $CaO-SiO_2$  binary and  $CaO-SiO_2-CaF_2$  ternary system; b) other slag system.[1]

The driving forces of the B and P removal from Si metal phase to slag phase is the equilibrium constants of the B and P removal reaction equations shown above and the concentration gradients of B and P in the bulk silicon to that at the interface between liquid slag and Si.

The distribution of boron was rearranged as the following equation:

$$L_B = \frac{(B)}{[B]} = K_1 \frac{\gamma_B \cdot a_{O^{2-}}^{\frac{3}{2}} \cdot P_{O_2}^{\frac{3}{4}}}{\gamma_{BO_3^-}} = K_1 \frac{\gamma_B \cdot a_{O^{2-}}^{\frac{3}{2}}}{\gamma_{BO_3^-}} \cdot \left( \frac{K_8 \cdot a_{SiO_2}}{a_{Si}} \right)^{\frac{3}{4}}$$

In order to achieve high high  $L_M$  at equilibrium, such experiments are set up to the optimum combination of  $P_{O_2}$  (being a function of  $a_{SiO_2}$ ) and basicity of the slag (being function of  $a_{O^{2-}}$ ).

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The two requirements (*i.e.* high  $p_{O_2}$  and  $a_{O^{2-}}$ ) are in conflict, because  $SiO_2$ , as an acidic component, increases the  $p_{O_2}$  but decreases the basicity of the slag. The observed dependence of  $L_B$  on slag composition in the above figures is explained by these competing effects. As the  $CaO:SiO_2$  ratio increases, the amount of free oxygen ion increases due to the dissociation of  $CaO$ , resulting in greater capacity for the slag to absorb boron oxide. On the other hand, this decreases the activity of  $SiO_2$  in the slag ( $a_{SiO_2}$ ), also lowering the  $p_{O_2}$ . As a result, the  $L_B$  increases at first with increasing  $CaO:SiO_2$  ratio, then decreases after reaching a maximum value, creating a negative parabola function against basicity. An exception to this was observed by Teixeira *et al.*, [4] where the refining took place under an air atmosphere. In that work, the amount of  $O_2$  in the system was always enough for boron oxidation, allowing the  $L_B$  to be continually increased by increasing the  $CaO:SiO_2$  ratio to create more free oxygen anions. Those researchers believed that the decreasing portion of the positive parabola curve in their  $CaO-SiO_2$  binary system was caused by the incorporation of boron into the silicate network in the region of high silica content.

The advantage of silicon production operation at KazSilicon is the injection of  $O_2$  into the liquid silicon during the slagging treatment, where high  $p_{O_2}$  and highly basic fluxes were locally established at the flux-Si interface. The injection of  $O_2$  gas also helps to stir the liquid slag and Si melt, decreasing the time to remove B and P from Si melt to liquid slag phase.

Several slag systems have been demonstrated during the KazSilicon pilot period and the slag were based on the following components:  $Na_2CO_3$ ,  $SiO_2$ ,  $CaO$ ,  $CaF_2$ ,  $BaCO_3$ ,  $Al_2O_3$ , and  $MgO$ . The advantage and disadvantage of different component are given:

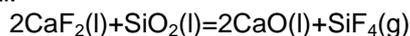
**$SiO_2$ -based slag:** First of all, the  $SiO_2$  containing slag can form silicate network in slag, which will prevent the heat loss from silicon melt; secondly, the existing  $SiO_2$  in slag can prevent the significant silicon loss from Si melt as slag, as the saturated  $SiO_2$  composition in the slag is constant, when there is more  $SiO_2$  initially in slag, less amount of Si melt is able to be oxidized to form  $SiO_2$ . However, the large amount of  $SiO_2$  in the slag increase the slag basicity significantly, also as a network former, the slag with large amount of  $SiO_2$  has a high viscosity, lowering the

speed of the ion mobility inside the slag, which may result in a longer operation time.

**$CaO/CaCO_3$ -based slag:** The most common basic slag used in the slag system. As a network modifier, it liberates the  $O^{2-}$  into slag forming slag complex with impurities, such as B and P. As shown in Figure 3, most of slag systems containing  $CaO$ .

**$MgO/BaO/BaCO_3$ -based slag:** Even though  $BaO$  has a high basicity, but its low optical basicity and further decrease of activity of  $SiO_2$  results in a small B distribution. However, the highest P distribution was found in  $MgO$ -Based slag [8] by Johnston and Barati.

**$CaF_2$ -based slag:** First, Adding  $CaF_2$  decreases the slag melting temperature, and temperature range at which the slag is liquid is expanded. Second, due to above expanded temperature range, the range of basicity also increases. Third, When  $CaO/SiO_2$  is low in slag, the reaction between  $CaF_2$  and silica forming  $CaO$  results in final  $CaO/SiO_2$  is higher than initial.



However,  $CaF_2$  addition significantly reduces B distribution [3, 6]. The work done by Luo shown in Figure 3 also confirmed this.[10] This is probably caused by the reduced silica in slag leading to low oxygen potential of the system.

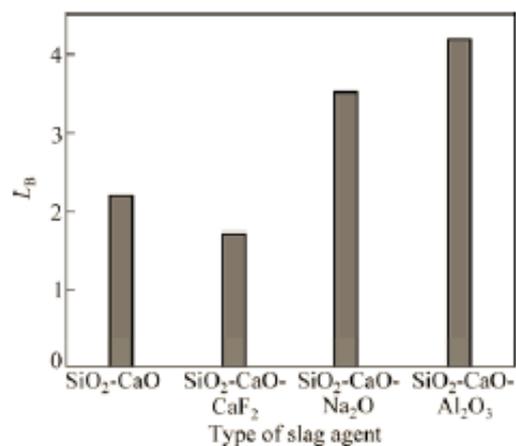


Figure 3. B distribution in different types of slag systems,  $CaO/SiO_2$  at 1.2[10]

**$Na_2O/Na_2CO_3$ -based slag:**  $Na_2CO_3$  decompose to  $Na_2O$  at temperature of  $850^\circ C$ . Basicity of  $Na_2O$  is higher than  $CaO$ , the addition of  $Na_2O$  leads to higher B distribution ratio (fig. 4).

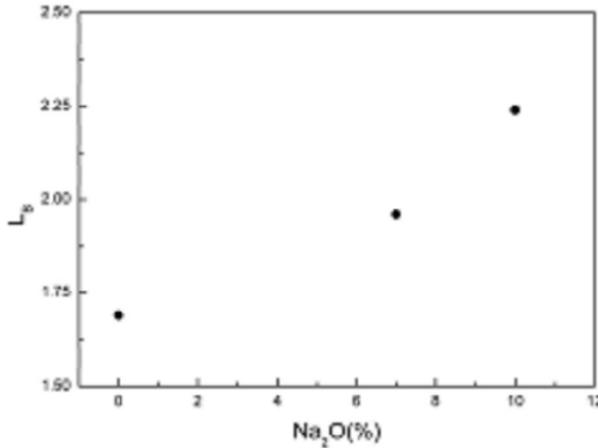


Figure 4 Effect of addition of Na<sub>2</sub>O on the L<sub>B</sub> for CaO-SiO<sub>2</sub> slags at 1550°C[3]

However, Na<sub>2</sub>O as a highly volatile substance at high temperature, it evaporates as fume. As a result, the longer slagging time and higher slagging temperature leads to a decrease in the content of Na<sub>2</sub>O in slag, decreasing B distribution.[10]

**Al<sub>2</sub>O<sub>3</sub>-based slag:** The main reason of adding Al<sub>2</sub>O<sub>3</sub> into slag is to prevent the attack on the furnace liner as most furnace liner is made of Al<sub>2</sub>O<sub>3</sub> based material (fig. 5). As Al<sub>2</sub>O<sub>3</sub> saturation percentage in the slag is constant, once there is Al<sub>2</sub>O<sub>3</sub> present in the slag initially, the amount of Al<sub>2</sub>O<sub>3</sub> that the slag can dissolve becomes less.

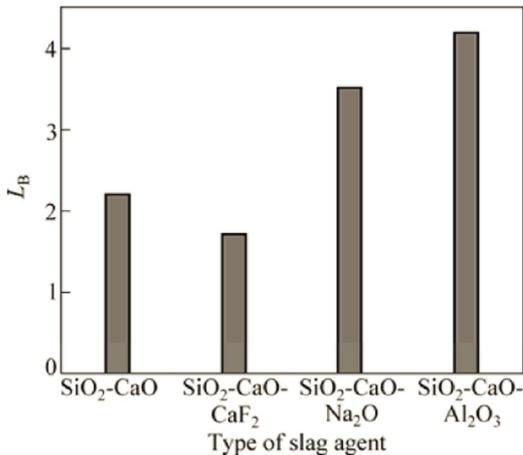


Figure 5. B distribution in different type of slag systems[10]

This causes the protection of the liner. It is also found that the addition of Al<sub>2</sub>O<sub>3</sub> in CaO-SiO<sub>2</sub> based flux results in the highest B distribution at 1500°C.

### 3 EXPERIMENTAL

The first step is production of MG-Si. The second step is about the slagging refining. The flow chart below show the production procedure for producing higher quality MG-Si:

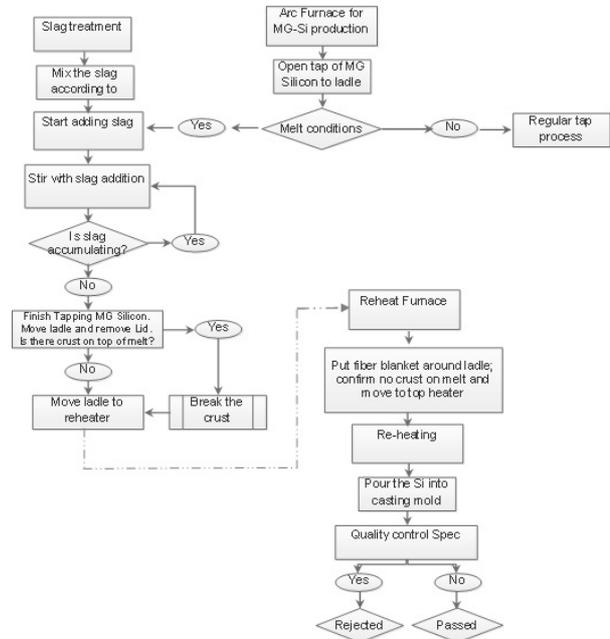


Figure 6. Flow chart of the slagging treatment at KazSilicon

The pre-mixed fluxes are added into the ladle according to the quality of the MG Silicon, after liquid MG-Si is poured into the ladle, which is then moved to the re-heating station. The liquid MG-Si and slags are heated in a reheat furnace. Once reached the designated temperature and refining time, the ladle is moved to the casting station. The liquid UMG-Si is poured into casting mould. Due to the density difference between liquid slag and Si, the slag floating on the top of liquid does not pour into the casting mould with the purified Si.

The average weight of the purified Si is around 1 metric ton (MT). The silicon samples, before and after slagging treatment, were analyzed by XRF and ICP-AES.

### 4 RESULTS AND DISCUSSION

#### 4.1 metallic elements removals

The slagging treatment results are listed below. The table below shows the Tap ID, the chemistry of the slag used under "Slag System", the ratio of slag to tapped Si, Al and Ca removal percentages.

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Tap ID	Slag System	slag/ta p Si	Al remov al %	Ca remov al %
239	Na <sub>2</sub> CO <sub>3</sub> -SiO <sub>2</sub>	18.54	97.46	93.87
252	Na <sub>2</sub> CO <sub>3</sub> -SiO <sub>2</sub>	4.55	80.17	95.87
255	Na <sub>2</sub> CO <sub>3</sub> -SiO <sub>2</sub>	4.62	95.07	93.63
260	Na <sub>2</sub> CO <sub>3</sub> -SiO <sub>2</sub>	5.13	94.42	95.62
262	Na <sub>2</sub> CO <sub>3</sub> -SiO <sub>2</sub>	13.33	98.18	99.48
344	Na <sub>2</sub> CO <sub>3</sub> -SiO <sub>2</sub>	10.81	95.21	95.16
348	Na <sub>2</sub> CO <sub>3</sub> -SiO <sub>2</sub>	13.64	98.64	98.70
264	Na <sub>2</sub> CO <sub>3</sub> -CaO-SiO <sub>2</sub> -CaF <sub>2</sub>	6.84	97.39	96.41
268	Na <sub>2</sub> CO <sub>3</sub> -CaO-SiO <sub>2</sub> -CaF <sub>2</sub>	6.43	97.52	95.85
269	Na <sub>2</sub> CO <sub>3</sub> -CaO-SiO <sub>2</sub> -CaF <sub>2</sub>	5.93	69.28	29.38
276	Na <sub>2</sub> CO <sub>3</sub> -CaO-SiO <sub>2</sub> -CaF <sub>2</sub>	11.69	98.01	92.09
287	Na <sub>2</sub> CO <sub>3</sub> -CaO-SiO <sub>2</sub> -CaF <sub>2</sub>	11.21	82.82	73.41
292	Na <sub>2</sub> CO <sub>3</sub> -CaO-SiO <sub>2</sub> -CaF <sub>2</sub>	10.43	98.02	90.78
294	Na <sub>2</sub> CO <sub>3</sub> -CaO-SiO <sub>2</sub> -CaF <sub>2</sub>	12.42	94.66	88.13
349	Na <sub>2</sub> CO <sub>3</sub> -CaO-SiO <sub>2</sub> -CaF <sub>2</sub>	13.64	98.53	95.84
371	Na <sub>2</sub> CO <sub>3</sub> -CaO-SiO <sub>2</sub> -CaF <sub>2</sub>	15.38	100.0	99.93
373	Na <sub>2</sub> CO <sub>3</sub> -CaO-SiO <sub>2</sub> -CaF <sub>2</sub>	12.63	96.06	95.90
300	CaO-SiO <sub>2</sub>	9.68	97.10	91.99
301	CaO-SiO <sub>2</sub>	7.84	71.45	41.26
315	CaO-SiO <sub>2</sub>	10.34	98.27	98.52
316	CaO-SiO <sub>2</sub>	9.92	97.98	99.18
317	BaCO <sub>3</sub> -CaO-CaF <sub>2</sub>	10.00	94.20	73.94
323	BaCO <sub>3</sub> -CaO-CaF <sub>2</sub>	16.10	99.44	93.04
324	BaCO <sub>3</sub> -CaO-CaF <sub>2</sub>	11.75	96.96	80.62
302	CaO-SiO <sub>2</sub> -CaF <sub>2</sub>	10.55	94.03	62.94
334	CaO-SiO <sub>2</sub> -CaF <sub>2</sub>	12.86	97.07	89.68
357	CaO-SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	16.67	86.24	85.39
365	CaO-SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	12.63	85.02	71.50
364	MgO-CaO-SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	12.50	96.86	98.46

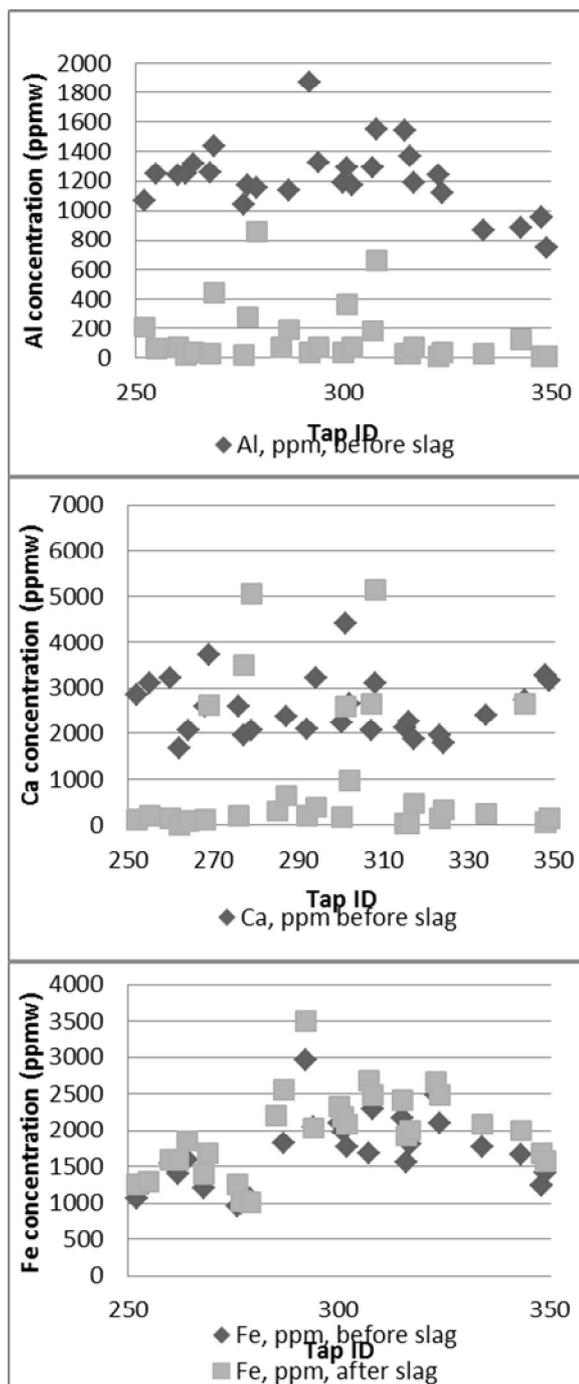


Figure 7. Impurity before and after oxidation refining. Tap: before refining, Cast: after refining.

The results show that slag treatment is very effective to remove metallic elements, such as Al and Ca, which are decreased under 300 ppm, but has little effect on Fe. All the slag systems used by KazSilicon but Al<sub>2</sub>O<sub>3</sub> containing slag system are effective on decreasing the content of Al in MG-Si by 97% and that of Ca by 98%. CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> based slag can remove Al and Ca by 85%. Compared to literature values of Ca

and Al removal percentage in CaO-SiO-Al<sub>2</sub>O<sub>3</sub> slag system at 50% and 85%, respectively,[10] the removal rate of Ca at KazSilicon is much higher.

Figure 7 above shows the drop in impurity levels for different metals (Al, Ca). It is clear that the slagging method is drastically reducing the amount of metal impurities in the silicon. As shown in Figure 1, Fe oxide is way more stable than Si oxide, it is very difficult to oxidize Fe to Fe oxide in Si melt initially. As a metallic element, unlike B and P forming Borate or phosphate linked structure, Fe ion in the slag does not bond with any slag network structure and Fe oxide in the slag can be easily reduced back to Si metal as metallic Fe. Unchanged Fe concentrations before and after slagging treatment in Figure 8 confirms this.

The thermodynamic and kinetic study of high temperature experiments is challenging. Compared to the lab scale slagging treatment experiment, it is extremely difficult to control the industrial scale process parameters precisely, such as the operational temperature and slag/metal mass ratio. Even though KazSilicon conducted more than 60 industrial scale trials, there are not many trials have similar operational parameters for the same slag system. Therefore, in the following sections, only limited data is presented for comparison.

**4.1.1 Effect of slagging treatment on Al and Ca**

As mentioned in Background section, oxidation alone can remove Al and Ca from liquid Si, to show the addition of slag further improve removal of Al and Ca, KazSilicon conducted few tests with the same refining time with/without slag. Table below shows the average Al and Ca removal percentages of all taps without slagging treatment, while in comparison to the removal percentage by slag treatment is low. The Al and Ca removal percentage increased in the purified Si by slagging treatment. The increasing removal efficiency of Al and Ca are mainly due to high affinity of slag to Al and Ca than Silicon.

	Al removal	Ca removal
No slag	77.73%	91.82%
Na <sub>2</sub> CO <sub>3</sub> -SiO <sub>2</sub> based slag	94.75%	94.63%

**4.1.2 Effect of mass ratio of Slag/Si melt**

As expected it was found that both Al removal and Ca removal percentages increase with an increasing mass ratio of Slag/Si melt as shown in the figures below. As seen in Figures 9

and 10 the effect of the mass ratio is different in different slag systems. The Ca removal percentage in Na<sub>2</sub>CO<sub>3</sub>-SiO<sub>2</sub> based slag does not increase as much as that in BaCO<sub>3</sub>-CaO-CaF<sub>2</sub>. This is mainly due the removal percentage of Ca in the Na<sub>2</sub>CO<sub>3</sub>-SiO<sub>2</sub> based slag is initially very high. Even with further increasing of mass ratio of Slag/Si melt, the incremental of Ca removal percentage is limited. The reason that Na<sub>2</sub>CO<sub>3</sub>-SiO<sub>2</sub> slag system can dissolve more Ca than BaCO<sub>3</sub>-CaO-CaF<sub>2</sub> is that Ca is oxidized as CaO, dissolving into slag. CaO is a silicate network modifier, and oxygen ion dissociated from CaO breaks the silicate network, resulting in the high capacity of Ca in the Na<sub>2</sub>CO<sub>3</sub>-SiO<sub>2</sub> based slag system than BaCO<sub>3</sub>-CaO-CaF<sub>2</sub> as in BaCO<sub>3</sub>-CaO-CaF<sub>2</sub> slag system, there is CaO in the slag initially, which limited the capacity of additional CaO that can dissolve into the slag system due to the fixed CaO saturated percentage. Al capacity in both slag systems are high as Al in liquid Si oxidized as Al<sub>2</sub>O<sub>3</sub>, which can easily form Alumino-silicate with SiO<sub>2</sub>, resulting in a high affinity of Al in both slag system (fig. 8, 9).

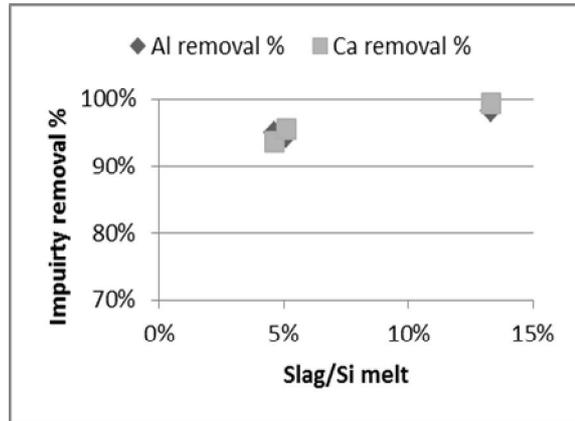


Figure 8. Al and Ca removal % in Si by slagging treatment vs slag/Si melt mass ratio for Na<sub>2</sub>CO<sub>3</sub>-SiO<sub>2</sub> based slag

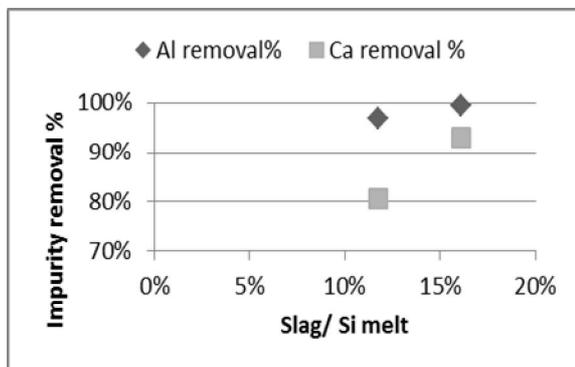


Figure 9. Al and Ca removal % in Si by slagging treatment vs slag/Si melt mass ratio for BaCO<sub>3</sub>-CaO-CaF<sub>2</sub> based slag

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### 4.1.3 Repeatability Test

Even though the parameters in the large industrial scale process are hard to control precisely, with more than 60 trials performed at KazSilicon, there are still some runs having similar operational parameters for repeatability test. It is important to repeat an experiment to make sure the results can be replicated. If one does an experiment and get a specific result but do the experiment again and get a different result that usually means there was a flaw in your original experiment and the results are not reliable. Repeatability of the slagging treatment was also studied during the slagging treatment trial period for Na<sub>2</sub>CO<sub>3</sub>-SiO<sub>2</sub> based slag and CaO-SiO<sub>2</sub> based slag. The results shown in the table below indicate that the slagging treatment performed in KazSilicon is repeatable. Since the slagging treatments were only repeated once, from a statistical point of view, more repeated tests are required to define the failure rate, which will be critical for production. The failure rate will be deeply investigated during the mass production.

slag ID	Al removal	Ca removal
Na <sub>2</sub> CO <sub>3</sub> -SiO <sub>2</sub>	95.07%	93.63%
Na <sub>2</sub> CO <sub>3</sub> -SiO <sub>2</sub>	94.42%	95.62%
CaO-SiO <sub>2</sub>	98.27%	98.52%
CaO-SiO <sub>2</sub>	97.98%	99.18%

### 4.1.4 Effect of Temperature on Impurity Removal.

As shown in Figures 8, Al and Ca removal percentages by Na<sub>2</sub>CO<sub>3</sub> containing slag are very high at the temperatures up to 1770°C. However, the KazSilicon furnace has very high efficiency, and once the production has no interruption, the temperature of the tap Si exceeds 1800°C. When the temperature increases, the removal of impurity should be increased, because the viscosity of slag decreases as the temperature increases, resulting in the increases in impurity mobility in the slag and in silica activity. All of these are conducive to the removal of impurity. However, as seen in Figure 10, impurity removal at low temperature is better than that at high temperature in the Na<sub>2</sub>CO<sub>3</sub> based slag system. This is partially caused by the evaporation of Na<sub>2</sub>O at high temperature, which decreased the slag basicity, resulting in significant decrease in Al and Ca removal percentages in Figure 11.

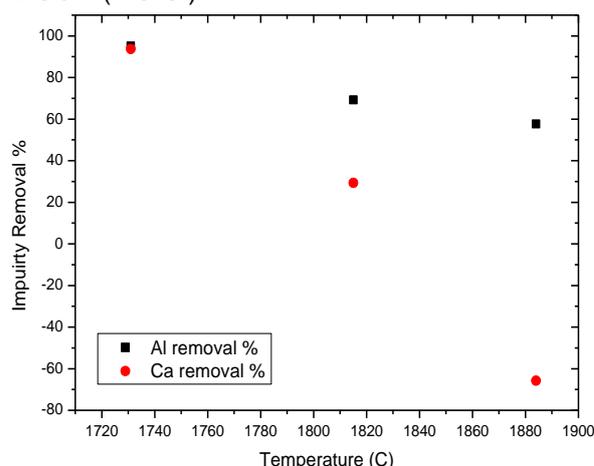


Figure 10 Al and Ca removal % in Si by Na<sub>2</sub>CO<sub>3</sub>-SiO<sub>2</sub> based slag at different temperature

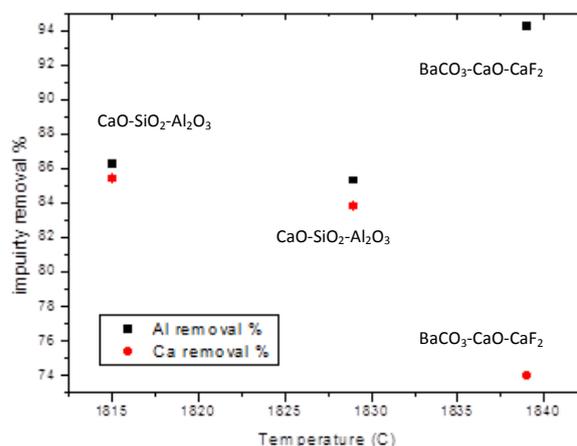


Figure 11 Al and Ca removal % in Si for different slag compositions

The above observation is agree with what reported by Luo *et al*[10], where the decrease of impurity removal occurred at 1600°C.

Slagging treatment results at KazSilicon show that at high temperature range, Al<sub>2</sub>O<sub>3</sub> and BaCO<sub>3</sub> based slag system has a high Al and Ca removal percentage than Na<sub>2</sub>CO<sub>3</sub> containing slags. However, due to safety concerns, KazSilicon can only use Al<sub>2</sub>O<sub>3</sub> based slag system at high temperature.

### 4.2 B and P removals

Due to the heavily contamination in the ICP-OES at KazSilicon, the measurement of B and P at Kazsilicon were not reliable. The B and P peaks were affected by large interferences due to other contaminants in the Silicon. The selected samples were sent to external lab for analysis using SIMS experiments in order to allow more accurate measurements because of the better energy resolution. Most of the purified

samples have shown B and P levels below 5 and 10ppmw respectively as shown in the table below.

	B	P
TAP #268, liquid Si	3.8	9.8
TAP #294, liquid Si	3.6	7
TAP #302, liquid Si	6.3	10.1
TAP #316, liquid Si	8.8	14
TAP #323, liquid Si	3.6	9.2
TAP #302, Si ingot	4.1	7.9

B and P removal efficiency is shown in the figure below. Tap #316 shows that slagging using the wrong chemistry does not show a very efficient removal of B and P. The best B and P removal efficiency of 64% and 68%, respectively was observed in Na<sub>2</sub>CO<sub>3</sub>-CaO containing slag.

In order to compare with literature data, which is usually presented by distribution ratio, removal efficiency of B and P were converted by

$$L = \frac{m_{Si}}{m_{slag}} \frac{R}{(1 - R)}$$

where R is removal efficiency. B distribution in CaO-SiO<sub>2</sub> system is around 1.2 and in CaO-SiO<sub>2</sub>-CaF<sub>2</sub> system is around 4. The value of B distribution reported by Luo *et al* [10] in CaO-SiO<sub>2</sub> and CaO-SiO<sub>2</sub>-CaF<sub>2</sub> are 2.3 and 1.8, respectively. The large scale slagging treatment result at Kazsilicon and literature data have the same order of magnitude, indicating that the slagging treatment conducted at KazSilicon is quite successful.

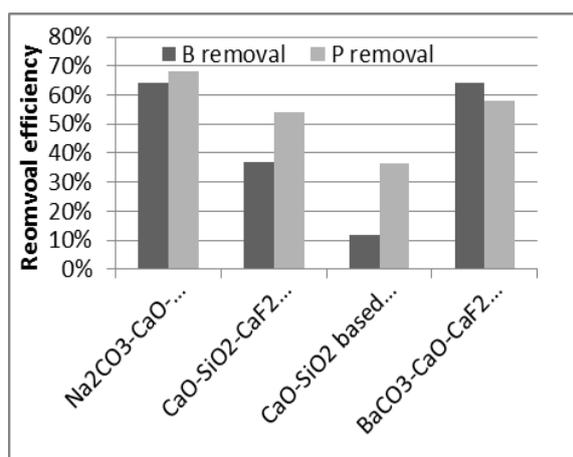
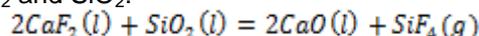


Figure 13 B and P removal % from MG-Si in different slag system

Compared to CaO-SiO<sub>2</sub> binary slag system, the addition of Na<sub>2</sub>CO<sub>3</sub> and CaF<sub>2</sub> into CaO-SiO<sub>2</sub> slag system increase both B and P removal efficiency. It is obvious that Na<sub>2</sub>O decomposed from Na<sub>2</sub>CO<sub>3</sub> with basicity higher than that of

CaO is used, resulting in a greatly improved basicity of slags, but also a better B and P removal efficiency. CaF<sub>2</sub> can decrease the melting temperature and the viscosity of the slag, and it is usually added in the slag when the operational temperature is low.

As mentioned in Background section the addition of CaF<sub>2</sub> into slag system usually results in a decrease in B and P removal. However, in current operational condition, the concentration of SiO<sub>2</sub> in slag is very high due to the O<sub>2</sub> injection into the Si melt. As a result, CaO/SiO<sub>2</sub> is lower than 0.8, due to the reaction between CaF<sub>2</sub> and SiO<sub>2</sub>:



CaF<sub>2</sub> reacts with silica forming CaO, increasing the basicity of the slag. The addition of CaF<sub>2</sub> provided a broader basicity range when compared to the binary CaO-SiO<sub>2</sub> slag system. With a combination of these two factors, the B and P removal efficiency is improved in the current slagging process.

BaCO<sub>3</sub>-CaO-CaF<sub>2</sub> slag system also shows a good B removal efficiency value. The reason is similar to the case of Na<sub>2</sub>CO<sub>3</sub> addition. As the basicity of BaO is higher than CaO, the addition of BaCO<sub>3</sub> increases the slag basicity, resulting in the improvement in B and P removal.

## 5 CONCLUSIONS

1) Slagging refining pilot production conducted at KazSilicon successfully remove a significant amount of impurities, such as Al, Ca, B and P from MG-Si produced by petroleum coke technology in industrial scale production. Compared to the literature data, the slagging treatment performed at KazSilicon demonstrated on large scale manufacturing ability to remove significant amount of B and P using the proper slag process. The highest removal efficiency of Al, Ca, B and P from MG-Si are 99%, 99%, 64% and 68%, respectively.

2) The pilot production experiments indicate the usage of Al<sub>2</sub>O<sub>3</sub> based slag system at high temperature can prevent the drop of impurity removal efficiency. Na<sub>2</sub>CO<sub>3</sub> based slag is one of the best slag candidate to use for purifying MG-Si.

3) Impurity removal efficiency increased with temperature and mass ratio of slag/Si melt because the viscosity of slag reduced and the mobility of slag enhanced, and increasing mass ratio enhance the total capacity of impurity in the slag phase.

## COST ADVANTAGE AND QUALITY ADVANTAGES IN THE LARGE SCALE MANUFACTURING OF METALLURGICAL SILICON (MG-SI)

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- A. Betekbaev** – Chairman of the Supervisory Board of «MC «KazSilicon» LLP, Kazatomprom, e-mail: [abetekbaev@kazatomprom.kz](mailto:abetekbaev@kazatomprom.kz).
- K. Ounadjela** – Doctor of Science, General Manager of Clean Power Innovation, the USA, California, the Silicon Valley, e-mail: [kamel@cleanpowerinnovation.com](mailto:kamel@cleanpowerinnovation.com).
- B. Mukashev** – Doctor of Science, Professor, Academician of NAS RK, e-mail: [mukashev2005@mail.ru](mailto:mukashev2005@mail.ru).
- D. Skakov** – General Manager of «MC «KazSilicon» LLP, e-mail: [skakovdm@gmail.com](mailto:skakovdm@gmail.com).
- V. Timoshenko** – Technical Director of «MC «KazSilicon» LLP, e-mail: [vtimoshenko@kazsilicon.kz](mailto:vtimoshenko@kazsilicon.kz).
- A. Pavlov** – engineer of PTD of «MC «KazSilicon» LLP, e-mail: [art\\_roll@mail.ru](mailto:art_roll@mail.ru).