Extraction Kinetics of Silicon, Aluminum, and Calcium from Dubersay Basalt by Electric Smelting

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Abstract: This article presents experimental results of extraction of silicon, aluminum into ferrous alloys and calcium into calcium carbide by electric smelting of basalt from Dubersay deposit. The studies were performed using thermodynamic simulation and electric smelting in arc furnace. The thermodynamic simulation was performed using HSC-5.1 software based on the principle of minimum Gibbs energy. The studied blend was smelted in one-electrode lined arc furnace. The experimental results of extraction of silicon, aluminum, and calcium from Dubersay basalt demonstrated that under equilibrium conditions, interaction of basalt with carbon and iron was accompanied by formation of CaSiO$_3$, Al$_2$SiO$_4$, FeSi, SiO$_2$, SIC, CaSi, Na$_2$SiO$_3$, SiO$_2$, SiC, CaC$_2$, CaO, Ca$_3$SiO$_3$, Al, Al$_2$O$_3$. During electric smelting of basalt it was detected that without lime silicon and aluminum were maximally extracted into alloy, and calcium into calcium carbide – in 30-45 min, herewith, the maximum extraction rate (76.5%) was observed for silicon extraction into alloy, and the minimum rate (65.3%) – for calcium extraction into carbide; when 25% of lime were added to basalt, the rate of calcium extraction into calcium carbide increased to 87.3% with simultaneous decrease in the rate of silicon and aluminum extraction into alloy to 71.4% and 60%; respectively; in order to achieve the rate of silicon and aluminum extraction into alloy of 76.1-76.8% and 70.0-72.4%, respectively, and of calcium into calcium carbide of 77-79.4% with production of calcium carbide of 235-239 dm$^3$/kg, the electric smelting of basalt should be performed with 7.3-11.2% of lime from basalt weight in 36.2-33.9 min.

Index Terms: basalt, calcium carbide, electric smelting, ferrous alloy.

I. INTRODUCTION

Basalt is the most abundant magmatic rock, it amounts to ≈30% of Earth surface area [1]. Nowadays basalt is used as construction and lining material, it is used for production of cast stone material, basalt fibers (for heat and sound insulating materials), basalt continuous fibers (for instance, for production of basalt fabrics, roadbed reinforcement grids, basalt pipes, vessels, acid resistant reinforcement, etc.) [2]-[12]. Nevertheless, resource potential of basalt is used insufficiently.

According to Daly [13], basalt is generally comprised of silicon oxide (49.06%), aluminum oxide (15.17%), calcium oxide (8.95%), and iron oxide (5.38% Fe$_2$O$_3, 6.37\%$ FeO). Hence, it should be considered as a challenging raw stuff not only for wide range production of basalt fibers (and items in their basis) but also for new products containing Si, Al, Cu, Fe. In order to expand fields of basalt application for production of competitive items, the authors propose the smelting technology of ferrous alloy and calcium carbide [14]. This method is based on the following reactions:

\begin{align*}
\text{(1)} \quad \text{CaO} + 2\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + 13\text{C} = 2\text{FeSi} + \text{CaC}_2 + 2\text{Al} + 11\text{CO}; \\
\text{(2)} \quad \text{CaO} + \text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe} + 8\text{C} = \text{FeSi} + \text{CaC}_2 + 2\text{Al} + 6\text{CO}; \\
\text{(3)} \quad \text{CaO} + 2\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe} + 10\text{C} = \text{FeSi}_2 + \text{CaC}_2 + 2\text{Al} + 8\text{CO};
\end{align*}

for which $\Delta G^0 = 0$ at 1465.1, 1819.7, and 1815.7°C, respectively (Table I).

| Temperature, $^\circ$C | Reaction 1 | Reaction 2 | Reaction 3 |
|-----------------------|------------|------------|------------|
| 1,000                 | 922.86     | 942.59     | 1,187.15   |
| 1,200                 | 526.04     | 713.67     | 891.93     |
| 1,400                 | 132.36     | 486.43     | 599.00     |
| 1,500                 | -71.03     | 369.67     | 453.39     |
| 1,600                 | -274.6     | 253.31     | 308.74     |
| 1,700                 | -477.6     | 137.58     | 164.87     |
| 1,800                 | -679.3     | 22.59      | 22.24      |
| 1,900                 | -880.1     | -91.92     | -119.7     |
| 2,000                 | -1,080.1   | -206.05    | -261.03    |
| 2,100                 | -1,277.3   | -317.59    | -399.72    |

*calculated by HSC-5.1 (Reaction Equations)

The main advantage of this technology is combined production of two products in one electric furnace. Reasonable course of this process should be based on extraction kinetics of silicon, aluminum, and calcium into end products. This article presents experimental results of extraction of silicon, aluminum in ferrous alloy and calcium into calcium carbide upon electric smelting of basalt from Dubersay deposit located in Aktyubinsk oblast, its resources are 10.8 mln t [15].

Revised Manuscript Received on August 20, 2019.

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II. METHODS

Algorithm The studies were performed using thermodynamic simulation and electric smelting in arc furnace. The thermodynamic simulation was performed using HSC-5.1 software based on the principle of minimum Gibbs energy [16].

Electric smelting of the blend was performed in one-electrode lined arc furnace. The bottom electrode was made of graphite block. A graphite crucible (d=6 cm, h=12 cm) was placed onto the bottom. The space between crucible and lining was willed with powdered graphite. The furnace top was covered with removable lid with holes for graphite electrode (d=3 cm) and gas discharge. Prior to smelting, the crucible was heated by arc during 20-25 min. Then the first portion of blend (200 g) was loaded in the crucible. Then it was smelted during 3-5 min, then the remaining blend (200 g) was loaded and smelted for required time. The furnace was powered by a TDZhF-1002 transformer. The required power was maintained by thyristor controller. Current was monitored by a Tangen 42L6 ammeter (accuracy rating: 1.5), and voltage by a Chint 42L6 voltmeter (accuracy rating: 1.5). After the electric smelting, the hot crucible was removed from the furnace and cooled in 5-6 hours. Then the graphite crucible was broken. Carbide and ferrous alloy were weighed and analyzed for Fe, Si, Ca, and Al.

Raw stuff and products of electric smelting were analyzed by scanning electron microscopy (JSM-6490LM (Japan)), atomic adsorption method (AAS-1IN, (Germany)). Concentration of Si+Al in the alloy was determined by pycnometry (on the basis of density) using equations published in [17].

The extraction rate of silicon and aluminum to the alloy was determined by the ratio of metal weight in the alloy to metal weight in the blend. The extraction rate of calcium into commercial calcium carbide (αCa, %) was determined as follows:

$$\alpha_{Ca} = \frac{G_{Cc} \cdot C_{CaC_2} \cdot 0.625}{G_{bas} \cdot C_{Ca(bas)} + G_{lime} \cdot C_{Ca(lime)}} \cdot 100$$

where $G_{bas}$, $G_{lime}$ and $G_{Cc}$ were the weights of basalt, lime, and calcium carbide, respectively, g; $C_{Ca(bas)}$ and $C_{Ca(lime)}$ were the calcium content in basalt and lime, respectively, fractions; 0.625 was the ratio of calcium atomic weight to calcium carbide molecular weight; $C_{CaC_2}$ was the CaC$_2$ content in commercial calcium carbide, fractions, determined as follows:

$$C_{CaC_2} = \frac{L}{372}$$

where L was the amount of calcium content, dm$^3$/kg (determined experimentally by the procedure in [18]), 372 was the acetylene amount (dm$^3$) evolved upon interaction of 1 kg CaC$_2$ with water.

Flowchart The studies were performed with Dubersay basalt, its analysis is illustrated in Fig. 1 and Table II. Coke contained 86% C, 4.9% SiO$_2$, 2.2% FeO, 1.5% CaO, 1.8% Al$_2$O$_3$, 1.1% H$_2$O, 2.5% were the rest. CaO content in lime was 92.8%, SiO$_2$ – 3.7%, Al$_2$O$_3$ – 1.5%, Fe$_2$O$_3$ – 1.5%, the rest – 0.5%. In steel chips the iron content was 98.3%.

Coke was taken in excess by 1.1 times from the required amount for total recovery of SiO$_2$ and Al$_2$O$_3$ to Si and Al, and Ca to CaC$_2$. Iron content was constant equaling to 5% of basalt weight.

III. RESULTS AND DISCUSSION

At the first stage of the studies, prior to electric smelting of basalt, the authors performed thermodynamic simulation of temperature influence on equilibrium quantitative distribution of substances in basalt–carbon–iron system. Fig. 2 illustrates quantitative distribution of substances containing Si, Ca, Al in Dubersay basalt–carbon–iron as a function of temperature (carbon content was 50% and iron content was 4% of basalt weight), obtained using HSC-5.1 software.

| Element | wt % |
|---------|------|
| O       | 45.18|
| Na      | 2.07 |
| Mg      | 3.64 |
| Al      | 6.62 |
| Si      | 18.07|
| P       | 0.1  |
| K       | 0.3  |
| Ca      | 7.19 |
| Ti      | 1.1  |
| Mn      | 0.28 |
| Fe      | 15.46|

Table II. Content of elements in Dubersay basalt determined by SEM

Fig. 1. SEM energy dispersion spectra of Dubersay basalt
It follows from Fig. 2 that in the temperature range of 1,500-2,500°C, under equilibrium conditions the interaction is accompanied by formation of CaSiO$_3$, Al$_2$SiO$_4$, FeSi, SiO$_2$, SiC, CaSi, Na$_2$SiO$_3$, SiO$_2$(g), CaSi$_2$, CaO, Ca$_2$O, Al$_2$O$_3$, Al, Al$_3$O$_5$. It can be seen in Fig. 2 that calcium carbide in the presence of lime is described as follows:

\[
\text{CaC}_2 \rightarrow \text{Ca}_2\text{O}_2 + 2\text{C}
\]

The observed decrease in the extraction rate of calcium into calcium carbide is related with its decomposition [18]: CaC$_2$=Ca$_2$O+$\text{C}_2$. Dubesay basalt contains less CaO than SiO$_2$, Al$_2$O$_3$. Hence, the amount of formed calcium carbide (due to combining CaO into calcium silicates and aluminates) does not exceed 130-150 dm$^3$/kg. In order to increase this amount, it is required to study the influence of CaO addition to basalt (in the form of lime) together with determination of its influence on extraction rate of Si, Al into alloy and Ca into calcium carbide. With this aim, the authors studied extraction kinetics of silicon, aluminum into alloy, calcium into calcium carbide in the presence of 25% lime of basalt weight. It can be seen in Fig. 4 that in the presence of lime, the extraction rate of calcium into CaC$_2$ increases to 87.3%. However, the extraction rate of silicon and aluminum in particular into alloy decreases to 71.44% and 60%, respectively. In the presence of lime, $\alpha_{\text{Ca}}$ into CaC$_2$ is maximum in 30 min, and $\alpha_{\text{Si}}$ and $\alpha_{\text{Al}}$ are maximum into alloy in 30-45 min of electric smelting. The amount of calcium carbide obtained upon basalt smelting in 30 min was 278 dm$^3$/kg. The influence of smelting time on extraction of metals into alloy and calcium carbide in the presence of lime is described as follows:

\[
\begin{align*}
\alpha_{\text{Si}} &= 14.65 + 4.0 \cdot \tau + 4.38 \cdot 10^{-2} \cdot \tau^2; \\
\alpha_{\text{Al}} &= 19.96 + 3.85 \cdot \tau - 4.46 \cdot 10^{-2} \cdot \tau^2; \\
\alpha_{\text{Ca}} &= 4.23 + 4.32 \cdot \tau - 5.05 \cdot 10^{-2} \cdot \tau^2.
\end{align*}
\]
Taking into account negative influence of lime on $\alpha_{\text{Si}}$, $\alpha_{\text{Al}}$ and positive influence on $\alpha_{\text{Ca}}$ and carbide amount, further study was performed using rotatable experiment design of the second order (the Box-Hunter method) [20]. The extraction rate of silicon, aluminum into alloy and calcium into calcium carbide was determined as a function of lime content (from 0 to 25%) and time (from 10 to 40). In accordance with [21], on the basis of 13 smelting runs by two-factor experiment matrix, the influence of lime and time on the extraction rate of silicon, aluminum into alloy and calcium into calcium carbide was determined.

Using the experimental results, the following adequate regression equations of the influence of electric smelting time ($\tau$, min) and lime (Lime, %) on specifications of electric smelting of basalt were obtained:

$$
\alpha_{\text{Si}} = -7.0 \cdot 0.86 + t + 4.84 \cdot \text{Lime} - 2.8 \cdot 10^{-3} \cdot t^2 + 6.89 \cdot 10^{-2} \cdot \text{Lime}^2 + 2.04 \cdot 10^{-5} \cdot t \cdot \text{Lime};
$$

(12)

$$
\alpha_{\text{Al}} = -15.3 \cdot 0.26 \cdot t - 4.56 \cdot \text{Lime} - 5.68 \cdot 10^{-4} \cdot t^2 - 5.56 \cdot 10^{-3} \cdot \text{Lime}^2 + 1.06 \cdot 10^{-6} \cdot t \cdot \text{Lime};
$$

(13)

$$
\alpha_{\text{Ca}} = -34.75 \cdot 0.57 \cdot t + 6.77 \cdot \text{Lime} - 8.52 \cdot 10^{-4} \cdot t^2 - 10.49 \cdot 10^{-3} \cdot \text{Lime}^2 - 2.65 \cdot 10^{-5} \cdot t \cdot \text{Lime};
$$

(14)

Using Eqs. 13-14, according to the procedure in [20], [21], 3D and 2D images of extraction rate of Si, Al into alloy and calcium into calcium carbide as a function of time of Dubersay basalt electric smelting were obtained (Figs. 5-7). It follows from Fig. 5 that $\alpha_{\text{Si}}$ (from 70% to 82.2%) is observed in the $\text{abcd}$ region, $\alpha_{\text{Al}}$ (from 70% to 77.1%) – in the $\text{peg}$ region (Fig. 6), and calcium extraction into calcium carbide (from 70% to 81.5%) – in the $\text{fklmno}$ region (Fig. 7). The $\text{peg}$ region (that is, for $\alpha_{\text{Al}}$) is characterized by the minimum variants (in terms of time and lime content) of compliance with the condition $\alpha_{\text{Al}} > 70\%$. Inside this region the $\text{zgx}$ region is highlighted (Fig. 6) which is constrained from left and below by the amount of 235 dm$^3$/kg (according to [22], calcium carbide in amount of 235 dm$^3$/kg is referred to the third grade), and from left and below – by $\alpha_{\text{Al}}=70\%$. Specifications for the end points of this region are summarized in Table III.

It follows from Table II that in order to achieve the rate of silicon and aluminum extraction into alloy of 76.1-76.8% and 70.0-72.4%, respectively, and of calcium into calcium carbide of 77-79.4% with production of calcium carbide of 235-239 dm$^3$/kg, the electric smelting of basalt should be performed with 7.3-11.2% lime of basalt weight in 36.2-33.9 min.
IV. CONCLUSION

The following conclusions can be derived from the experimental results of extraction of silicon, aluminum, and calcium from Dubersay basalt:

1. Under equilibrium conditions, the interaction of basalt with carbon and iron is accompanied by formation of CaSiO$_3$, Al$_2$SiO$_3$, FeSi, SiO$_2$, SiC, CaSi$_2$, Na$_2$SiO$_3$, SiO$_2$(s), Si$_3$N$_4$, CaC$_2$, CaO, Ca$_3$O$_7$, Al$_2$O$_3$, Al, Al$_2$O$_3$.

2. It has been detected upon electric smelting of basalt that:
   - without lime, silicon and aluminum are maximally extracted into alloy, and calcium into calcium carbide – in 30-45 min, herewith, the maximum extraction rate (76.5%) is observed for silicon extraction into alloy, and the minimum rate (65.3%) – for calcium extraction into carbide;
   - when 25% of lime are added to basalt, the rate of calcium extraction into calcium carbide increases to 87.3% with simultaneous decrease in the rates of silicon and aluminum extraction into alloy to 71.4% and 60%; respectively;
   - in order to achieve the rate of silicon and aluminum extraction into alloy of 76.1-76.8% and 70.0-72.4%, respectively, and of calcium into calcium carbide of 77-79.4% with production of calcium carbide of 235-239 dm$^3$/kg, the electric smelting of basalt should be performed with 7.3-11.2% of lime from basalt weight in 36.2-33.9 min.

ACKNOWLEDGMENTS

This work was supported by the Committee of Science, Ministry of Education and Science of Kazakhstan, project No. AP05130683 titled Integrated production technology of ferrous alloys and calcium carbide from nonconventional raw stuff and technogenic substances containing highly abundant elements.

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