Light Metals

PRODUCTION OF ALUMINUM-SILICON ALLOYS FROM

SAND AND CLAY IN HALL CELLS

Alton T. Tabereaux and Curtis J. McMinn
Reduction Research Division
Reynolds Metals Company
Sheffield, Alabama

Sand and clay mixed with metallurgical alumina were reduced in alumina reduction cells to produce silicon-aluminum alloy. It was demonstrated that these methods of producing silicon-aluminum alloy were viable alternates to the use of silicon produced in electric-arc furnaces. Additions of SiO_2 containing material to the reduction cell resulted in loss of production and decreased ampere efficiency; typically, a 0.5% ampere efficiency loss was found to occur per weight percent silicon metal produced from the silica material. A procedure or practice is discussed for the planned and carefully controlled operation of reduction cells using additions of silica by effectively regulating the total distributive oxide concentration in the electrolyte.

Introduction

Aluminum casting alloys containing up to 17% silicon are becoming more important as automotive manufacturers must decrease weight of their product. Most of the silicon used in aluminum alloys is produced in electric arc furnaces and subsequently alloyed with aluminum either in furnaces or reduction cells. While direct reduction of SiO_2 in electrolytic cells does not replace this method it is an alternate method that may be economical under some situations. These situations include silicon alloy producing aluminum reduction plants remote from electric furnace silicon supply, especially when these plants have surplus reduction capacity. When market pressures increase the price of silicon metal this process may become an economical alternate to using purchased silicon.

The use of clays in the production of aluminum alloys utilize a low cost and domestic source of a limited amount of alumina. Blending is necessary because of the high silica content of clays.

Process Description

Closely monitored tests made in reduction plants produced data to evaluate the process. Commercial alumina reduction cells were operated on various mixtures of silica materials and metallurgical aluminum.

Current efficiency for the tap group of cells was determined for the overall period of operation from metal production and total ampere hours. Metal pad inventories of the cells were determined at the start and end of each test by manganese and copper dilution analysis.[1] A voltage integrator and recorder installed on each cell provided daily, average cell voltage information and the number, and time, of anode effects per cell. Routinely, the temperature of the electrolyte was measured three times per week and bath samples were analyzed for NaF/AlF_3 ratio three times per week. Periodic measurements were made of anode and cathode current distribution, voltage drops of anode and cathode and ledge buildup.

Feed Materials and Alloys Produced

Some of the silica containing materials tested at pilot and/or plant scale included sand, quartzite rock, and clay. Typical chemical compositions of sand and clays used in tests and the resulting alloys produced are given in Table I. Alloys produced from clays reflect that higher levels of Fe_2O_3 and

Table I. Typical Composition of Silica Materials and Alloys Produced from Them

	White Clay*	Tan Clay**	Red Clay*	Sand**
Silica Materials:				
Al_2O_3, w/o	48.02	49.09	43.10	0.89
SiO_2	48.50	47.09	48.38	98.66
Fe_2O_3	1.68	1.11	6.66	0.37
TiO_2	1.68	2.31	1.50	0.025
K_2O	0.17	0.64	0.12	0.05
P_2O_5	0.03	0.072	0.05	0.005
CaO	ND	0.10	ND	0.01
MgO	ND	0.23	ND	0.02
LOI, 1000°C	1.06	0.32	1.07	ND
Alloys Produced:				
Si, w/o	10.0	9.4	7.10	9.3
Fe	0.21	0.30	0.87	0.22
Ti	0.45	0.37	0.29	0.05
Cu***	0.007	0.003	0.018	0.017
Mn***	0.005	0.002	0.008	0.05
Zn	0.03	0.02	0.033	0.02

*   Pilot scale tests

**   Commercial reduction cells

***   Added for inventory purposes

ND = Not determined

TiO_2 in these materials result in considerably higher impurity levels.   In a similar manner, higher levels of K_2O, P_2O_5, and CaO, and MgO in the clay material result in higher equilibrium levels of these impurities in the electrolyte.

The high purity sand used in the test was normally purchased as masonry sand from local deposits in the region of the reduction plant.   The sand had been washed and contained about 5% moisture when received.   The moist sand was dried on the outer crust before feeding.

Clays can be used as a source of both silica and alumina. White kaolinic clays with low titania and iron oxide selected from deposits in Georgia are adequate for direct reduction.   A cal- cined, kaolinic clay containing 100% less than 14% mesh of the following composition was specified.

SiO_2	–	45-50%
Al_2O_3	–	40-50%
Fe_2O_3	–	0.2 to 1%
TiO_2	–	<1.9%
K_2O	–	<0.3%

Because it was uneconomical to upset production to dig clay from low TiO_2 pits a clay containing higher levels of impurities was substituted as shown in Table I.   The clay was purchased in 50 lb bags to facilitate handling and to eliminate the need of weighing out four 150 lb additions per day that would be required to maintain the specified 9% silicon content of the cells. The particle size of the clay used in the test is as follows: +100 mesh, 76.23%; +200 mesh, 5.80%; +325 mesh, 11.03%; -325 mesh, 6.93%.

Theoretical Reduction Reactions

When alumina dissolves in cryolite it breaks up into positive and negative ions.   The passage of line current between the carbon anode and the aluminum cathode in commercial reduc- tion cells causes the Al^{3+} ions to flow to the metal pad where they are discharged to make metal.   The oxygen part, actually combined in a more complex negative ion, flows to the carbon anode, and is also discharged.   It reacts with anode carbon to make and release anode gas, carbon dioxide.   The overall reaction is generally described by the following equation:

$$Al_2O_3 + 3/2C = 2Al + 3/2\ CO_2 \qquad (1)$$
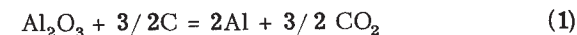
Thus, the electrolysis of silica in a cryolitic flux might be expected to proceed in an analogous reaction:

$$SiO_2 + C = Si + CO_2 \qquad (2)$$

However, in laboratory tests it has been shown by Grjotheim, et. al.[2] that when the Na_3AlF_6 - SiO_2 mixture is in contact with aluminum, silica reacts with aluminum according to the equation:

$$3SiO_2 + 4Al = 2Al_2O_3 + 3Si \qquad (3)$$
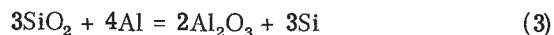
Bullough[3] discloses that this process proceeds stoichiometrically and is useful for the direct preparation of silicon-aluminum alloys in commercial cells.

Faraday Requirements and Methods
Used to Circulate Current Efficiency

More electrical current is required to produce silicon from silica than is required for aluminum. Theoretically, it requires 1353 ampere hours to produce one pound of aluminum and 1733 ampere hours to produce one pound of silicon. Thus, 1.281 times as many ampere hours is required to reduce silica as compared to alumina.

In the production of silicon alloys from silica current efficiency, or ampere efficiency, it is taken to be:

$$C.E., \% = \frac{Actual\ Net\ Production}{Maximum\ Theoretical\ Production} \times 100 \qquad (4)$$

where the term "net production" means metal derived from the reduction of oxides. This includes the aluminum content of a silicon alloy, and that portion of the silicon not derived from the direct addition of elemental silicon.

The maximum theoretical production per 24 hour period of a cell reducing silica is:

$$MTP = \frac{1774.5 \times I}{100 + 0.281\ (\%Si)} \qquad (5)$$

Where, I = cell current expressed in KA and, %Si = percent silicon in net production from silica.

Possible Production of SiF_4

The silicon recovery balance from silica in commercial cells is nearly always greater than 95%. This quantitative conversion indicates that little silicon is lost from the bath as volatile SiF_4, or as silicates deposited in the ledges. These results are in good agreement with those also observed by Grjotheim[2]; that SiO_2 losses as SiF_4 from cryolite fluxes occur only when alumina is absent, or at very low alumina concentrations.

Experimental

Operating Problems

The results of plant tests indicated that there was little loss in production for short periods (for one month or less) on sand additions in the production of 3% Si alloy. Minor operating problems were encountered in the production of 6% Si alloy, which became more difficult in the production of 9% Si, or higher, alloys. Thus, practicing the reduction of silica materials for the production of silicon alloys has often been found to be difficult due to the following conditions:

1. The direct addition of silica often results in the formation of such heavy ridges or deposited solids along the bottom of the cells near the anode that they interfere with the cells operation.

2. The cells are more susceptible to develop anode grounds, especially around the edges.

3. High cell voltages are required to burn off the anode grounds.

4. At high silica additions, the crust is soft, porous, and supports little pressure.

5. Changes in the electrolyte's composition occur with the addition of silica.

6. The cells may require constant attention of potman and supervisor.

Efficiency

The addition of silica to commercial cells for the purpose of producing Si alloys results in lower current efficiencies than theoretically predicted, as shown in Figure 1. The alloy production is lowered by 0.5 to 0.8% for each percent silicon alloy made by direct reduction of silica.
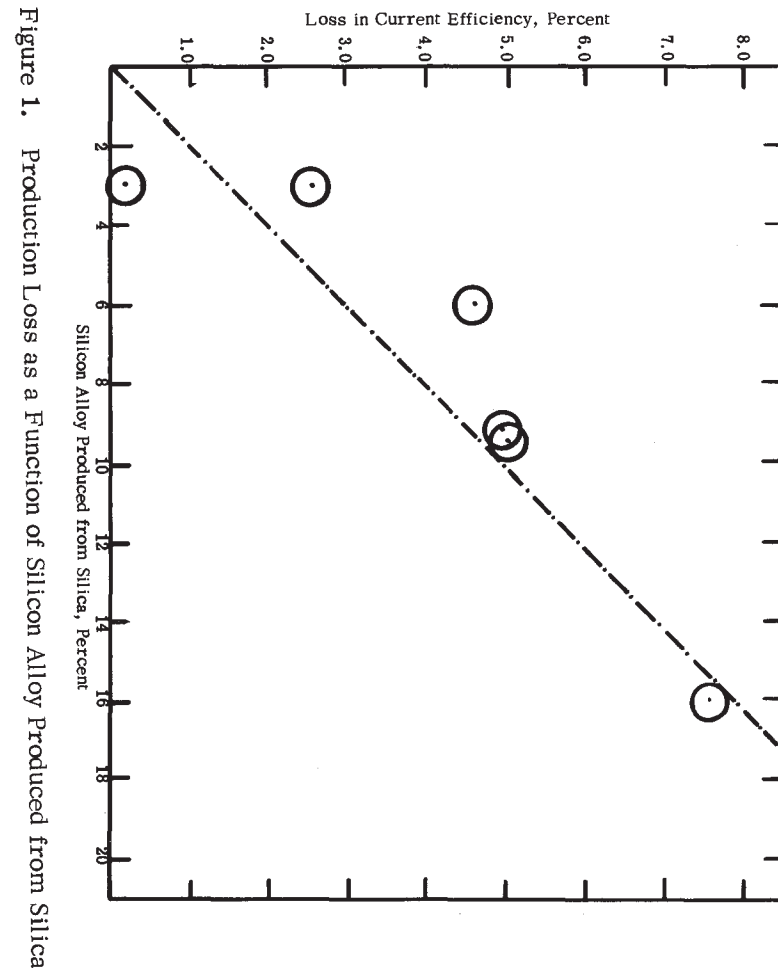
Modified Operation Practices

Oxide Addition Control

To ensure control of ledge formation and muck buildup in cells producing silicon alloys from silica materials, a program of total oxide control was developed.[4] Basically, the program controls the amount, manner, and timing that silica and alumina are added to reduction cells. An outline of procedures followed for the production of 16% silicon alloy from sand is given in Table II, in which approximately 400 pounds of sand per day is required to maintain the specified silicon alloy content at 75 KA.

The sand was distributed in the following manner.

1. Around 8:30 A.M., 100 pounds of sand was placed on both sides of the Soderberg cell.

2. The sand was spread over the crust and swept up against the anode so it would have a chance to be preheated before the sides were worked.

3. The sand was broken in with a reduced amount of alumina at 10:00 A.M. on the front side and at 2:00 P.M. on the back side of the cell.

4. After the 2:00 P.M. work, 100 pounds of sand was placed on both sides of the cell.

5. The sand was spread on the crust and swept up against the anode.

6. The sand was broken-in with a reduced amount of alumina at 6:00 P.M. on the front and at 10:00 P.M. on the back side of the cell.

Figure 1. Production Loss as a Function of Silicon Alloy Produced from Silica

Table II. Producing 17% Silicon Alloy – Soderberg Reduction Cell – (24-Hour Cycle of Operation)

Time	Operation		Volts (V)	Temperature (°C)	Al_2O_3/SiO_2 Ratio	NaF/AlF_3 Ratio
0600	Break in alumina only	Continuing opportunity to reduce SiO_2 content of bath and ridges, Melting out ridges.	4.7	948	5	1.43
0730	Spread 100 lb of high-grade sand on the crust with loose alumina, on both sides and close to the anode	Supplying one-half of daily silicon requirements for drying, preheating and mix; δ with alumina. Next to anode, so as to fall to metal-bath interface rather than to sidewall ledges.	4.75	950	13	1.45
0830	Tap and lower anode	Remove 2 days' production. (~2,480 lb). Just prior, total oxide very low.	4.72	948-940 →946	13-6 →2.5	1.39
1000	Break crust at front side of pot to feed alumina and silica	Replenish oxides. Supply SiO_2 for reaction to Si. Approx. 200 lb of aluminum silicate removed from solution in 1/2 hr				
1400	Break crust at back side of pot to feed alumina and silica	Replenish oxides. Some dissolution of silicate separated in previous break	4.80	950	2-4	1.43
1500	Spread 100 lb of sand along both sides of the anode					
1800	Break front side	Replenish oxides, dissolved and tying on ledges and bottom	4.75	945	2-4	1.44
2200	Break back side	Ditto. Clean up of undesirable solids.	4.80	952	5-10	1.44
0200	Scheduled break; not performed	Necessary oxides supplied from continuing dissolution of alumina silicates.		965	10-15	1.45
0517	Anode effect	Establishes "end point" to dissolution of alumina silicates	20	965		1.44
0600	Break in alumina only	dissolution of alumina silicates				

Ledge Control

The total oxide content of the cell was depleted by omitting scheduled alumina breaks:

1. Beginning with the 2:00 A.M. break, the cell was <u>not</u> worked until it had experienced an anode effect.

2. If after a sufficient amount of the time the anode effect was found to be occurring shortly after the 6:00 A.M. scheduled work, then the cell would be worked at 6:00 A.M.

In accordance with this aspect of the program, we controlled both the silica and alumina content of the cell with respect to a 24-hour period to minimize the separation and buildup of undesired materials on the ledges and bottoms of the cells. Adequate opportunity must be provided for the periodic dissolution of silica and alumina in the cell to avoid excessive accumulations.

For purposes of controlling the formation of ledges, the feeding of alumina and silica was omitted entirely at the final two regularly scheduled crust breaking operations during each daily cycle of operation. This action has an important impact on several aspects on the pot operation. As shown in Figure 2 this action daily depletes the total oxide content of the electrolyte. The temperature of the molten cell contents rises about 5-15°C as the oxides are depleted after feeding and crust breaking operations are omitted. This increase in temperature, along with the lower oxide content, promotes the dissolution of the separating materials associated with silica being added to the bath. If the total oxide content is depleted sufficiently for an anode effect to occur, the cell undergoes even further heating.

Under some conditions such as low silica additions, the lowering of the oxide content and consequent heating may be sufficient to control the ledging conditions while avoiding the disruption of operation and extra voltage caused by an anode effect. Under more severe conditions of ledging, such as might be caused by extra heavy additions of silica, it is advantageous to continue the oxide depletion until an anode effect occurs. While this interruption of the breaking and feeding schedule, and the subsequent increase in cell temperature cause a small loss in production, the advantages concerning the control and stabilization of the ridge geometry and limitation of the amount of insoluble muck or sludge under the metal pad have been found to outweigh the disadvantages.
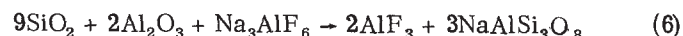
Bath Ratio Control

There is substantial evidence to document the mechanism that when silicon is introduced into the bath it reacts very rapidly with cryolite and alumina to produce cryolite and bath soluble silicates. Our laboratory work has demonstrated that there is a quantitative, permanent decrease in the NaF/AlF_3 ratio with the addition of SiO_2 to a non-electrolyzing cryolitic bath containing alumina. However, no similar decrease in ratio occurs if alumina is absent in the bath. In actual plant tests, the decrease in NaF/AlF_3 ratio has been found to be cyclic around SiO_2 additions to the cell, as shown in Figure 2, with the application of an electrolysis current. A "generalized" relationship between bath ratio and SiO_2 content is shown in Figure 3. In the absence of alumina, the addition of SiO_2 to bath oftentimes liberates a significant quantity of volatile SiF_4.[2]

The temporary reduction of bath ratio, NaF/AlF_3 is interpreted as a bath reaction between silica, alumina, and cryolite to form a cryolitic soluble silicate and generate aluminum fluoride; for example,

$$9SiO_2 + 2Al_2O_3 + Na_3AlF_6 \rightarrow 2AlF_3 + 3NaAlSi_3O_8 \qquad (6)$$

The soluble silicate compound is then gradually reduced chemically or electrolytically, and cryolite is regenerated.

If bath samples are taken for ratio control shortly after silica is broken into the electrolyte, the bath ratio will constantly read lower than that for a pure metal cell, and, as a result, the aluminum fluoride consumption rate will appear to be lower than that for pure metal cells.

With large additions of silica to cells, i.e., hypereutectic Si alloy production of bringing cells up to grade, the addition of Na_2CO_3 may be required to control the ratio.

Economics

Silicon alloy produced from silica feeds to reduction cells becomes economically competitive with silicon alloy produced from electric furnace silicon under some circumstances. These circumstances involve the availability of silicon metal at a price not inflated by a limited supply situation and the presence of surplus aluminum capacity. Reduction plants producing silicon alloy remote from electric furnace silicon capacity may also find the direct reduction of silica to be an attractive alternate.
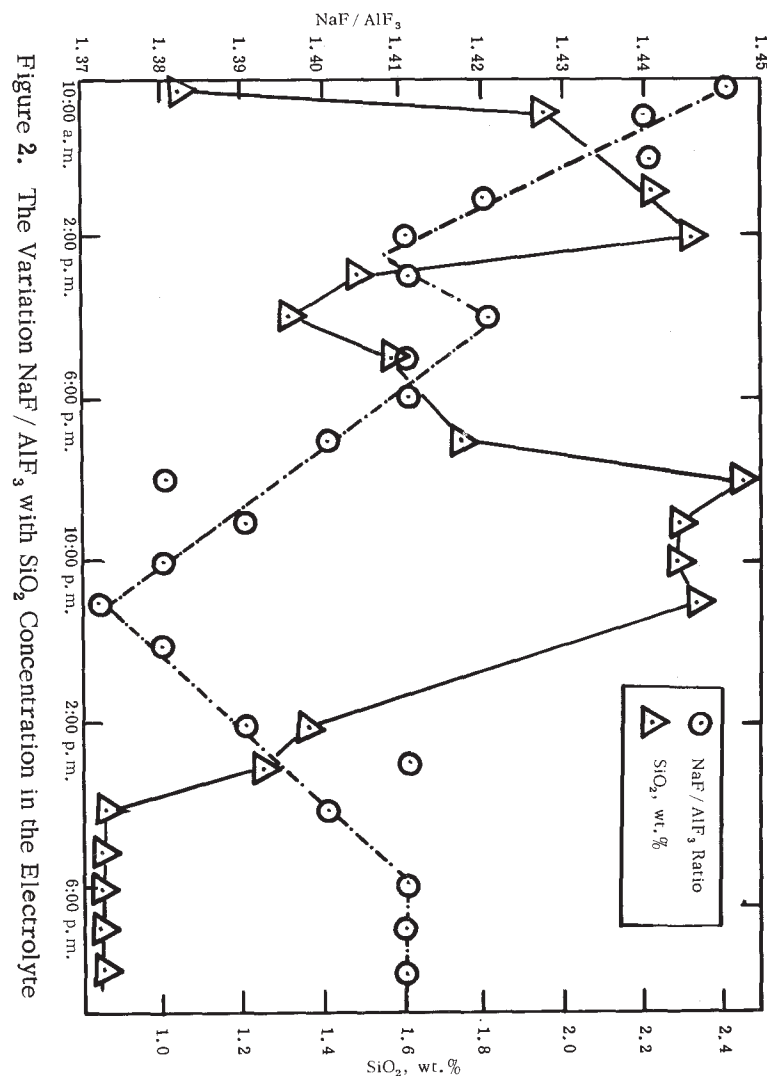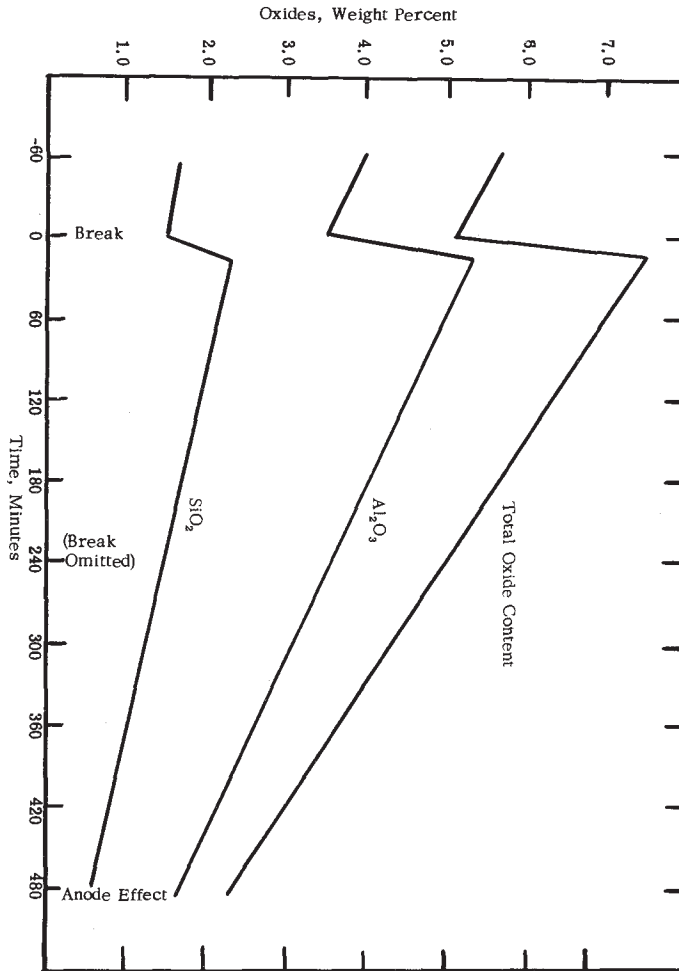

Figure 2. The Variation NaF/AlF_3 with SiO_2 Concentration in the Electrolyte

Figure 3. Typical Oxide Profile from Break to Anode Effect

Summary

It has been demonstrated that high purity sand and high grade calcined clay can be reduced directly in industrial alumina reduction cells to produce commercial aluminum-silicon alloys. The pot ledges and muck can be effectively controlled and stabilized by practicing a method of total oxide concentration control. The production from the cell producing silicon alloy from silica will be less than that for a comparable alumina reduction cell producing pure metal, or silicon alloy from metallurgical silicon additions. Typically, a 0.5 ampere efficiency loss per percent silicon alloy produced from silica is experienced. The process is viewed as an alternate method of silicon alloy production that is economically attractive in some situations.

References

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