Aluminothermic production of silicon using different raw materials

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ABSTRACT

Silicon is a vital element in many products today, such as electronic components, solar devices, high-quality alloys, and many others. The growing global demand highlights the need for the development of sustainable production methods to meet this demand as an alternative to the current carbothermic reduction, submerged arc furnace (SAF) based process. An alternative to this is the aluminothermic reduction of quartz in a CaO-SiO_2 slag, which not only reduces direct carbon dioxide emissions but also promotes the utilisation of secondary raw materials such as quartz fines, aluminium dross and scrap as well as secondary alumina (SA) from dross recycling.

In the current study, the effects of SA and CaF_2 additions to slag on the resulting metal composition and metal yield were explored. Results were compared with thermodynamic simulations using FACTSage© 8.1.

Experimental results show that, in agreement with thermodynamic simulations, the silicon content of the alloy is increased, while the Ca is decreased for starting slags where CaO-SiO_2 is partly replaced by CaF_2. Similarly, the addition of SA to the initial slag results in an alloy with a higher silicon content.

INTRODUCTION

Silicon is the second most abundant element in the Earth's crust and one of the most important elements in high-tech applications. Traditionally, metallurgical-grade silicon (MG-Si), typically containing 96-99 % Si, is produced by reducing silicon dioxide (SiO_2) with carbon in a submerged arc furnace (SAF) (Schei, J. Tuset and Tveit, 1998). In this process, a mixture of quartz (crystalline SiO_2) and carbon (coke, coal, charcoal, and/or wood chips) is heated to produce silicon. The energy is supplied through electrodes, and it takes 10-13 MWh to produce one tonne of silicon. Using carbon materials as reductants leads to emissions primarily of carbon dioxide (approximately 5 tonnes CO_2 per tonne of silicon produced), NO_x, SO_x, methane, polycyclic aromatic hydrocarbons (PAH), etc. (Kero, Grådahl and Tranell, 2017). In addition to the high greenhouse gas (GHG) emissions and high energy demands, requirements on the quartz used in the process need to be met. Aside from purity, there are strict requirements for size since particles that are too small reduce gas permeability in the furnace, increasing the likelihood of blow-outs due to gas build-up, which means that sand of high purity cannot be used in the traditional production process (Schei, J. K. Tuset and Tveit, 1998).

Aluminium, having a stronger affinity for oxygen than silicon, may hence be utilised as a reducing agent for the production of silicon, and this process can be considered a viable alternative to the carbothermic process. The SisAl process, based on the aluminothermic reduction of silica in slag, aims to produce silicon in a more environmentally beneficial way (Tranell, Safarian and Wallin, 2020). This is achieved by eliminating the need for primary carbon reductants and lumpy quartz raw materials and using residues from the silicon and aluminium industries instead. No carbon use means no direct emission of CO_2 and other gaseous pollutants.

In the SisAl process, SiO_2 can be used in the form of fines to produce slag, which means that less costly quartz sand can also be used as a SiO_2 source. By introducing an aluminium source (end-of-life scrap, dross) for the reduction of SiO_2 in CaO-SiO_2 slag, silicon alloy and Al_2O_3-CaO slag are produced according to the following equation:

$$SiO_{2(in\ SiO_2-CaO\ slag)} + \frac{4}{3}Al_{(liq)} \rightarrow Si_{(liq)} + \frac{2}{3}Al_2O_{3(in\ Al_2O_3-CaO\ slag)} \quad \Delta H_{1550°C} = -174.8\ \frac{kJ}{mol}$$

The generated slag is isolated from the metal, and the CaO and Al_2O_3 may be separated through a hydrometallurgical technique. CaO can be reintroduced back into the SisAl process, while the Al_2O_3 can be sent to primary aluminium production. Due to lower operating temperatures and an exothermic reduction reaction, the SisAl process consumes less energy compared to the carbothermic reduction in SAF.

A diverse range of waste byproducts is generated in the aluminium sector. Dross is a byproduct created during the handling of liquid alloy and is a mixture of Al alloy and oxides as well as some amount of carbides, nitrides, etc) and is formed as the melt oxidises. The quantity of waste material produced during the process of aluminium production is influenced by factors such as the quality and type of raw materials, operation conditions, the operator's skill, the kind of furnace utilised, and the dimensions, types, and techniques of alloying (Lazzaro, Eltrudis and Pranovi, 1994; Yoshimura *et al.*, 2008). Approximately 15-25 kg of dross is produced for every tonne of molten aluminium (Liu and Chou, 2013).

The primary objective of the present study was to investigate the impact of various input materials on the overall process, with a particular emphasis on the final products. This study includes an examination of the suitability of aluminium byproducts, such as dross and secondary alumina from treated dross obtained from Befesa Alumino, Spain, as reductants and additions in the process of aluminothermic production of silicon in terms of alloy composition. Recovery of materials in dross at Befesa is made through two cycles; in the first, the aluminium contained in the dross is recovered in a salt-based rotary furnace process, producing aluminium alloys, and in the second, recycling of salt slags, the waste that was traditionally discarded in landfills is recovered, transforming them into secondary raw materials, applicable in different industrial sectors. The recovered high-alumina fraction, in the following called secondary alumina (SA), contains some amount of residual fluorine, as discussed below.

The addition of CaF_2 to silicate slags typically decreases the viscosity and lowers the melting temperature (Park, Min and Song, 2002). As such, it was of interest to investigate the effect of limited fluorine additions on the SisAl process and its product compositions.

EXPERIMENTAL PROCEDURE

Overview of experimental procedure

The study on the impact of different input materials and process parameters on the overall process of aluminothermic production of silicon is organised into two subsections, as shown in the flowchart (FIG 1).

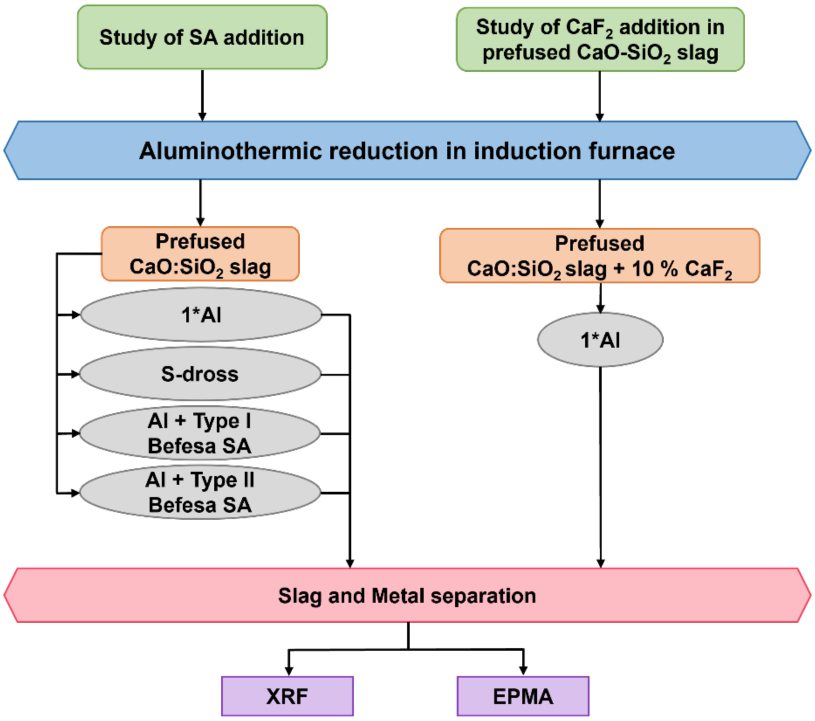

FIG 1 – The flowchart representing an Overview of the experimental procedure.

Materials

The pre-fused slag utilised in this study as a SiO_2 source had a CaO: SiO_2 ratio of 1.018. A fine fraction of dross (denoted S-dross), with particle size ≤ 5 mm, which contains 30% Al and 70% Al_2O_3, and pure aluminium (~ 99 % pure) was acquired. Two different SA samples were used along with pure aluminium as a reductant in the study of SA addition. The chemical composition of the materials used is presented in TABLE 1.

TABLE 1 - Composition of materials used in the present study.

Species	*Material composition (%)*		
	Prefused CaO-SiO_2 slag	**Befesa Type I SA**	**Befesa Type II SA**
CaO	49.9	2.76	3.56
MgO	0.42	7.69	6.14
SiO_2	49.00	4.97	10.57
Al_2O_3	0.43	75.20	67.07
Fe_2O_3	0.15	2.14	2.39
K_2O	0.03	0.90	1.14
SO_3	0.03	~	~
Cl	~	0.82	0.59
CuO	~	0.65	0.82
F	~	0.85	2.40
MnO	~	0.34	0.35
Na_2O	~	1.18	2.48
NiO	~	0.04	0.05
P_2O_5	~	0.09	0.10
TiO_2	~	0.95	0.76
ZnO	~	0.25	0.35
S	~	0.07	0.11
Cr_2O_3	~	~	~
ZrO_2	~	~	~
SrO	~	~	~
BaO	~	~	~
Co_3O_4	~	~	~

Apparatus and procedure

The aluminothermic reduction tests in this work were carried out in an Induction Furnace (75kW, 3000Hz). Each set of experiments utilised three small-sized resin crucibles, which were placed within a single large crucible and then inserted into the furnace. The inner sides and the base of the crucible were wrapped with graphite paper to prevent input from interacting with the graphite and to facilitate the effortless removal of the final product from the crucible. A C-type thermocouple was used to measure the temperature. The pre-fused slag (with CaF_2 in the second set of experiments) and reductant mixture were kept in crucibles, heated to a selected temperature, and held for a specific time. Throughout the experiment, argon gas was continuously purged to maintain an inert environment inside the system.

The experimental matrix of the present study is shown in TABLE 2. Prior to the experiment, dross, SA, and pre-fused CaO-SiO_2 slag were dried to remove all the moisture content. Pure aluminium was used along with Befesa SA in relative weights to mimic the same Al:Al_2O_3 ratio as that in the S-dross.

TABLE 2 - Experimental matrix of the present study.

Study	***Type***	***Expt No***	***SiO_2/slag source***		***Reductant/addition***			***Process parameters***	
			Prefused CaO:SiO_2 slag (g)	**CaF_2 (g)**	**Pure Al (g)**	**S-dross (g)**	**SA (g)**	**Temp (°C)**	**Holding time (min)**
Study of SA addition	**Pure Al**	1	141.9	-	41.58	-	-	1650	30
		2	141.6	-	41.49	-	-	1650	30
	S-dross	1	100.03	-	-	87.7	-	1700	60
		2	100.03	-	-	87.7	-	1700	60
		3	100.02	-	-	87.7	-	1700	60
	Al + Befesa Type I SA	1	100.03	-	26.46	-	82.08	1650	60
		2	100.05	-	26.66	-	82.00	1650	60
		3	100.03	-	26.40	-	82.05	1650	60
	Al+ Befesa Type II SA	1	100.02	-	26.60	-	92.03	1650	60
		2	100.17	-	26.65	-	92.15	1650	60
		3	100.02	-	26.58	-	92.05	1650	60
Study of CaF_2 addition in prefused CaO-SiO_2 slag	**Effect of CaF_2**	1	90	10	25.98	-	-	1650	60

Characterisation

EPMA

Metal samples were investigated using a JXA-8500F Field Emission Electron Probe Microanalyzer (EPMA). Backscattered electrons were used for sample imaging to visually represent different phases in the metal sample. EPMA's focus was on determining the elemental distribution and composition of silicon metal produced. Wavelength dispersive X-ray spectrometer (WDS) helped in performing elemental analysis of the different phases, while energy-dispersive X-ray spectrometer (EDS) was used over a particular area to determine an estimate of the element distribution of the different main elements.

XRF

Samples from the 'Study of CaF_2 addition in prefused slag' were also analysed using the X-ray fluorescence (XRF) technique at Degerfors Laboratorium AB in Bruksparken, Sweden. The slag and alloy samples were analysed using Thermo Fischer Scientific's ARL 9900 Series XRF device. The samples obtained from tests using pure Al and S-dross were analysed at RWTH, IME-Process Metallurgy and Metal Recycling, Aachen, Germany, using the RFA Omnian 37 / S via combustion method. Similarly, the Department of Geoscience and Petroleum (IGP) at NTNU in Trondheim, Norway, conducted an analysis of the samples obtained from trials using Befesa Type I and Type II SA.

Theoretical calculations - FactSage©

Thermodynamic simulations were performed using the software FactSage©, version 8.1 (by Thermfact Ltd. and GTT-Technologies) with databases FToxid and FTlite (*FactSage Summary of Databases*, no date).

RESULTS AND DISCUSSION

Results from SA addition experiments

This section gives details regarding the observations derived from experiments conducted using different Al sources. These observations encompass the resulting product's physical characteristics, the alloy's yield, and its composition.

Physical structure

This section presents the variations in the physical structure and appearance of aluminothermic reduction products obtained using different reductants.

It was observed that the structure of almost all the samples upon dissection exhibited a consistent pattern: a hemispherical Si alloy located at the uppermost part, with a slag layer positioned beneath the silicon metal (FIG 2). However, in some products, the silicon alloy was not observed at the top. In those products, the silicon metal was slightly below the top portion, entirely encircled by slag in every direction. When pure aluminium was employed as a reducing agent, the resulting product consisted entirely of a silicon alloy at the uppermost section and a slag at the bottom (FIG 2A). In the experiment where S-dross was used as a reductant, tiny drops of silicon alloy were seen above the topmost silicon part, as depicted in FIG 2B. The slag obtained was greenish brown in colour, which deviated slightly from the slags produced in experiments involving alternative reductants. XRF analysis of the slag revealed that the amount of Si in the slag from the trial with S-dross is relatively lower than that using pure Al and Befesa SA, which can be the reason for such appearance of slag. When SA, both Type I and Type II were utilised as a reductant, the topmost part was not entirely covered with silicon alloy. Observations revealed the presence of circular silicon alloys encased by slag. In one sample from the trial involving Al+Type II SA as a reductant, the silicon alloy was found to be positioned slightly below the top layer (FIG 2D). XRF analysis of SA identified several other impurities like Cl, CuO, F, Fe_2O_3, K_2O, and MgO. These impurities might have hindered the rapid reduction reaction at 1650 °C and the non-uniform deposition of the reduced Si alloy.

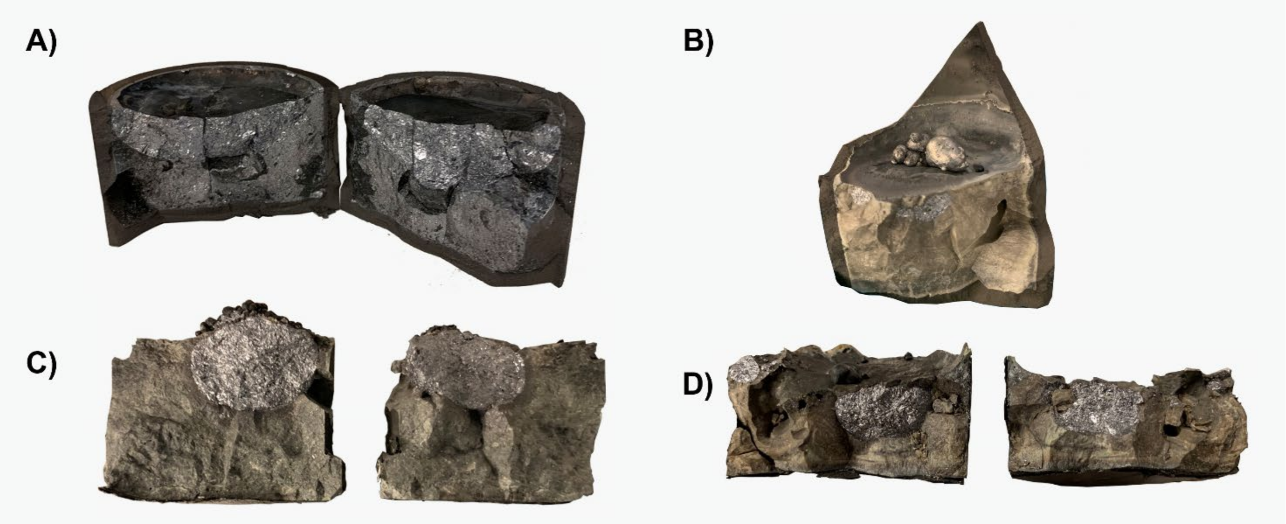

FIG 2 - Different structures of products obtained from aluminothermic reduction with the use of: A) pure Al, B) S-dross, C) Al +Type I SA, and D) Al +Type II SA.

Metal yield and mass loss

The loss in mass was calculated from the difference between the total input feed and output. The amount of silicon alloy yielded/added Al unit from each crucible, where different reductants were used, was measured. The percentage mass loss and the average amount (from three parallels) of Si per unit Al reductant produced using different reductants are shown in FIG 3.

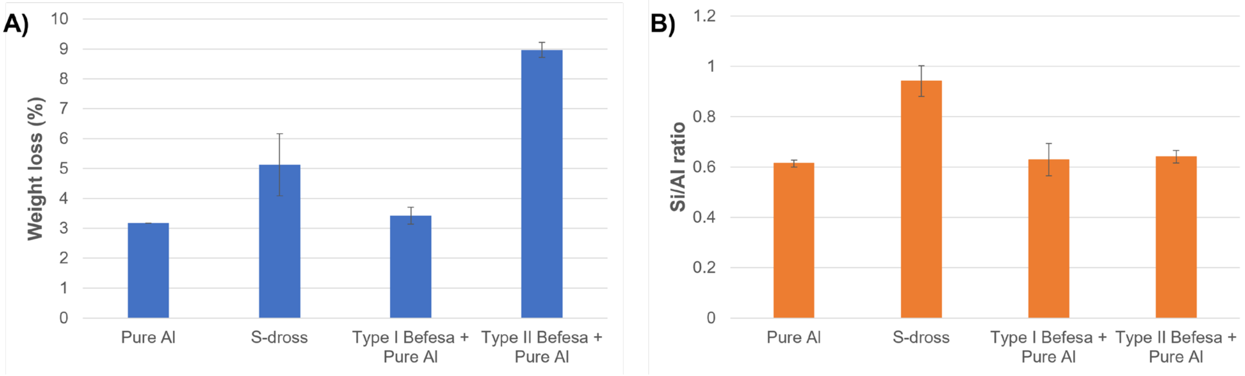

FIG 3 – A) Mass loss, and B) Si/Al ratio in experiments using different reductants. The values shown for reductant are the average of three trials conducted, except for pure Al, where values represent the average of two trials.

The Si/Al ratio, when the reductant used was S-dross, was higher than that yield obtained in all other experiments, while the trials using SA gave a comparatively similar but slightly higher metal output than the experiments using pure Al. Many small silicon droplets were present in different locations of the slag, making it difficult to collect the entire silicon alloy produced and consequently leading to comparatively high metal loss.

Loss in weight was considerably higher when SA were used. Since SA samples contain volatiles (alkali, F, etc) evaporation is expected to be higher for these materials.

Chemical composition

FIG 4 displays the predicted chemical composition of metal and slag by FactSage$^{©}$ and the EDS results for metal and XRF results for slag as mean values of three areas measured in each of the three crucibles, in which different reductants were used.

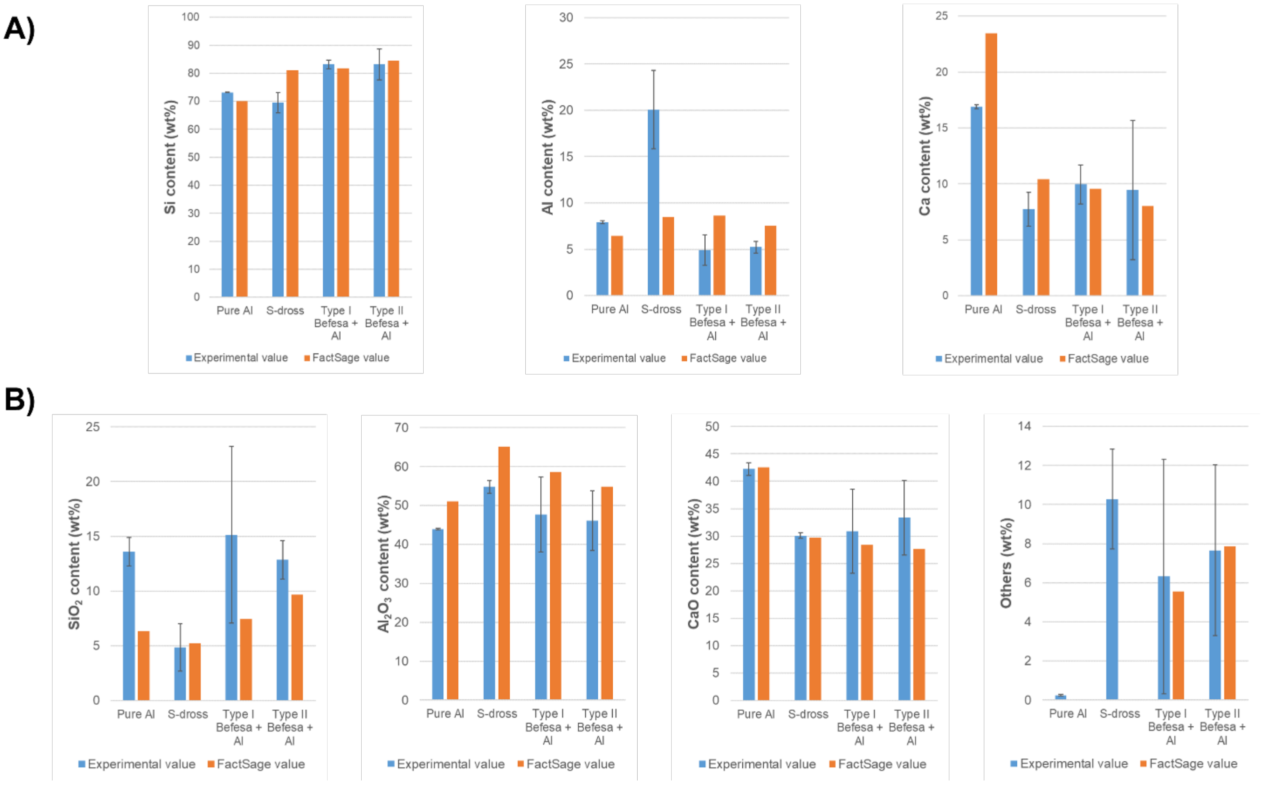

FIG 4 - The chemical composition of metal and slag obtained from experiments utilising different reductants, compared with the chemical composition based on FactSage© simulations. The given experimental values represent the average of three trials for each experiment, except for the one with pure aluminium as a reductant, where values represent the average of two trials.

The composition of metal samples from each crucible was analysed with EDS. The samples produced in experiments employing pure aluminium had a higher Ca content and lower or similar Al content than other samples, which mostly aligned with the observed pattern in the FactSage© simulation. The reverse result was obtained from experiments where S-dross was used, i.e., the content of Al was higher, and the content of Ca was lower. While the concentration trend for the produced metal in each experiment aligns with the simulation pattern, the most significant deviation in concentration is observed for S-dross, i.e., Si content is lower while Al content is much higher than predicted. This occurrence may be attributed to the composition of S-dross. The metallic Al content in S-dross was found by dissolving it in a NaCl-KCl-CaF_2 salt melt at 800˚C, a method with certain inaccuracy. Those values are taken for Al content for FactSage© calculation, which may, due to the heterogenous nature of dross, have affected the variation between experimental and predicted values. By using the two types of SA as additions to metallic Al, a metal with a higher Si content and a lower Al and Ca content was obtained compared to the metal obtained using pure Al.

An XRF analysis of SiO_2, Al_2O_3, and CaO content in the slag was conducted to examine the composition of the slag formed in experiments utilising different reductants. The remaining slag contained various impurities such as Cl, Mg, P, K, Fe, etc. No significant differences were seen while comparing the SiO_2, Al_2O_3, and CaO content in these samples from trials with different reductants. However, the composition of SiO_2 in slag samples from experiments using S-dross as a reductant was somewhat lower than the SiO_2 content present in other samples. As in the case of metal samples, the concentration trend aligns well with the FactSage© simulation, with a slight deviation in concentration values compared to the predicted ones.

BSE images

EPMA analysis of metal was conducted to provide backscatter electron imaging of the phases present. A significant difference in phase composition was not observed, as most of the EPMA results for metal showed similar phases (FIG 5A-D). Regardless of the type of reductant used, three distinct phases were consistently seen in all metal samples: Si, Si_2Al_2Ca, and Si_2Ca. Agreeing with the higher Si content measured by XRF, the presence of the Si phase was more prominently observed in BSE images of metal samples from trials with SA Type I and Type II. In the metal samples obtained from experiments using S-dross as a reductant, traces of $Si_{13}AlMnFe_4$ were observed, resulting from impurities in the dross.

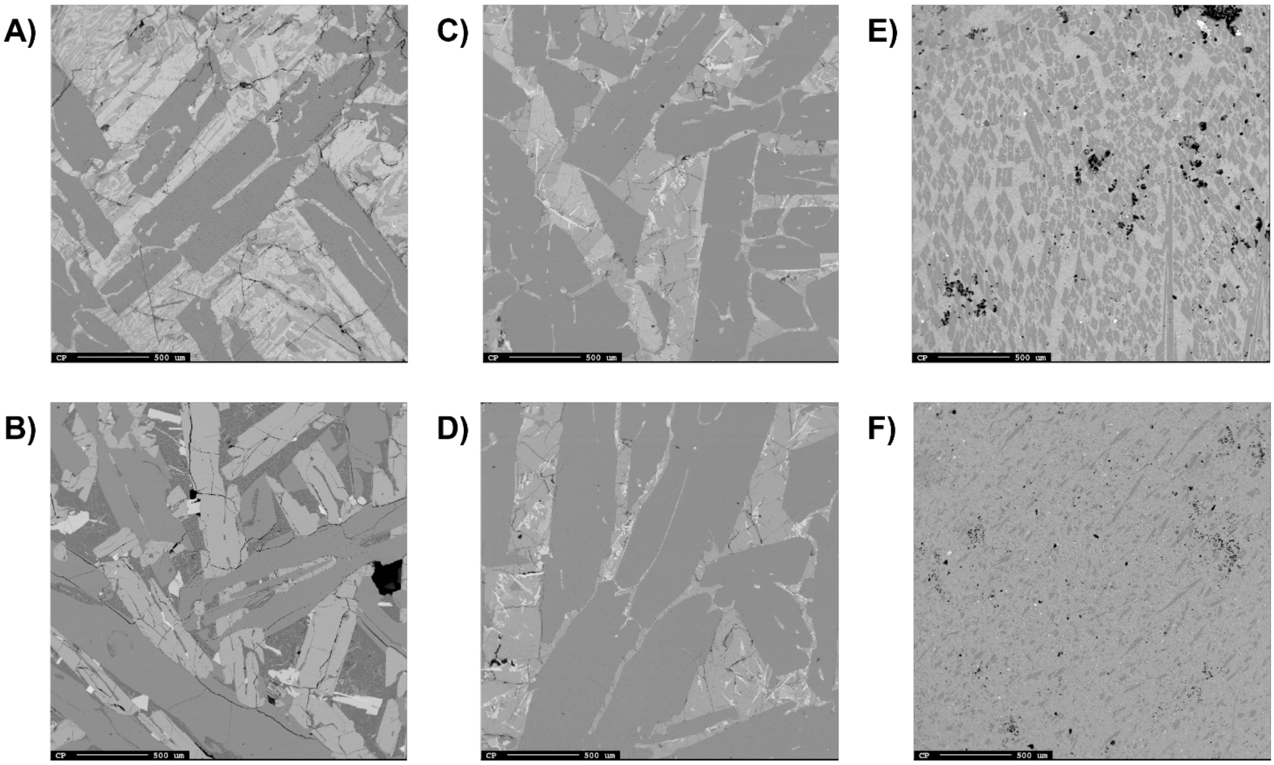

FIG 5 - BSE-image of: A) metal from Pure Al experiment, B) metal from S-dross experiment, C) metal from Type I SA + Pure Al experiment, D) metal from Type II SA + Pure Al experiment, E) slag from Type I SA + Pure Al experiment, and F) slag from Type II SA + Pure Al experiment.

The BSE images of the slags obtained from experiments using two different reductants, Type I SA and Type II SA, revealed the presence of two distinct phases (FIG 5E and FIG 5F). One phase, characterised by a darker appearance, mainly consisted of Al_2O_3-CaO, with Al_2O_3 being the predominant component, while the second phase, appearing lighter in colour, was primarily composed of CaO-Al_2O_3, with CaO being the dominant constituent. Small concentrations of SiO_2 (lighter) were rarely seen on BSE images of slag samples from trials with Type II SA, as EDS analysis revealed the composition of SiO_2 to be much lower compared to slag from experiments with Type I SA.

Results from experiments using CaF_2

The results of an aluminothermic reduction experiment in which a set concentration of CaF_2 was added to the slag included observations of its physical structure, the metal yield determination, and the chemical composition of the alloy and slag produced. A comparison was also made between an aluminothermic reduction experiment using CaF_2 in slag and an experiment without using CaF_2. Furthermore, this study's findings encompass comparing the composition of metal produced and simulated composition using FactSage© software.

The product obtained from the experiment using CaF_2 in pre-fused slag with stoichiometric aluminium as a reductant exhibits a similar structure to a product from the experiment without CaF_2 (FIG 2A). A rigidly structured product contains hemispherical-shaped silicon alloy at the top and heavily dense bluish-grey slag at the bottom, as shown in FIG 6.

FIG 6 - Physical structure of the product obtained from the experiment using CaF_2 in prefused slag and pure aluminium as a reductant.

A loss in mass and amount of Si per unit Al reductant, compared with the experiment without using CaF_2, are shown in FIG 7A. Compared with experiments with stoichiometric Al and rec slag without CaF_2, weight loss has been significantly lower in experiments using CaF_2. Si yield from the product is similar for both cases, as a stoichiometric reductant in the same amount was used in both.

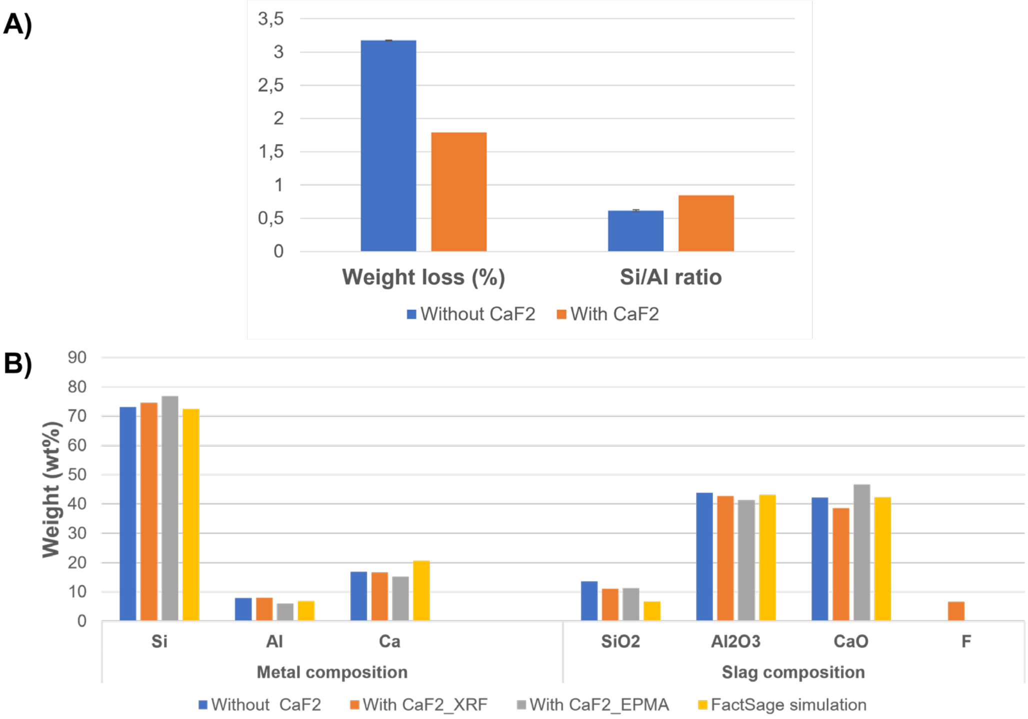

FIG 7 – A) Mass loss and metal yield, and B) chemical composition of metal and slag obtained from the experiment using CaF_2 in prefused slag compared to FactSage© simulation values, and the metal and slag composition obtained from the experiment without CaF_2.

The slag and metal obtained from this experiment were subjected to both XRF and EPMA analysis, and results were compared with the experiment without using CaF_2 and also with FactSage© simulation values, as shown in FIG 7B. When compared to the experiments without CaF_2, minor differences in metal and slag composition were seen, i.e. a slight increase in Si content while the Al and Ca content in metal decreased in the experiment where CaF_2 was used. In the case of slag, the results are similar to experiments without CaF_2; however, SiO_2 and Al_2O_3 contents were slightly lower. When comparing XRF and EPMA results, the only difference was a slightly lower concentration of CaO in slag in the XRF analysis results. The XRF analysis of the slag obtained from this experiment indicates the presence of 6.63 weight % of F.

The experimental results closely resemble the predictions made by the FactSage© simulation but with a slightly elevated Si concentration and reduced Al and Ca content in the metal. The same is the case with the content of SiO_2 in the slag, but the opposite is true in the case of CaO, where the FactSage© simulation predicted a lower value than the one obtained by the EPMA analysis.

Backscattered image obtained from EPMA for metal sample obtained in this experiment is shown in FIG 8.

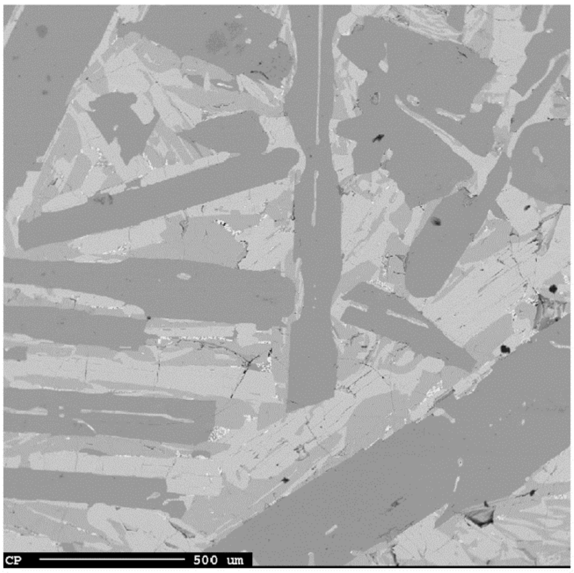

FIG 8 - BSE image of metal obtained from an aluminothermic reduction experiment in which CaF_2 was added to the silicate slags.

Three dominant phases have been identified in metal, similar to what we observed in the metal produced in experiments without CaF_2. The portion of dark-coloured Si is relatively equal in both cases, which is expected considering the similar Si content observed in XRF analysis results. Si_2Ca and Si_2Al_2Ca phases have been abundant, whereas only a few minor phases of impurities such as Fe, Mn, and Mg have been detected.

CONCLUSIONS

The primary aim of this study was to assess the feasibility of producing Si via an aluminothermic reduction process, focusing on achieving a high yield and minimising the calcium content. This study focused on investigating the impact of several factors on the aluminothermic reduction process, including the usage of different aluminium byproducts as reductants/additions and the influence of calcium fluoride.

Using SA combined with pure aluminium as a reductant resulted in a slightly higher purity of Si alloy than using other reductants. When pure aluminium was used as a reductant, the alloy produced had a higher concentration of Ca. When S-dross was added as a reductant, the situation was reversed, but the Al concentration was elevated. The dross contains a significant amount of Al_2O_3, so its use resulted in an increase in the concentration of Al_2O_3 in the slag.

Results from the study of CaF_2 addition also showed constructive results in obtaining pure Si. A small mass loss and high metal yield were observed from the experiment using pre-fused slag with 10% CaF_2. Si content in metal has been increased with the use of CaF_2. At the same time, Al and Ca content has been reduced, which is a favourable outcome.

ACKNOWLEDGEMENTS

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REFERENCES

FactSage Summary of Databases (no date). Available at: https://www.crct.polymtl.ca/fact/documentation/FSData.htm (Accessed: 30 December 2023).

Kero, I, Grådahl, S and Tranell, G, 2017. Airborne Emissions from Si/FeSi Production, *JOM*, 69(2):365–380.

Lazzaro, G, Eltrudis, M and Pranovi, F, 1994. Recycling of aluminium dross in electrolytic pots, *Resources, Conservation and Recycling*, 10(1):153–159.

Liu, N W and Chou, M S, 2013. Reduction of secondary aluminum dross by a waste pickling liquor containing ferrous chloride, *Sustainable Environment Research*, 23(1):61–67.

Park, J H, Min, D J and Song, H S, 2002. The effect of CaF_2 on the viscosities and structures of $CaO\text{-}SiO_2(\text{-}MgO)\text{-}CaF_2$ slags, *Metallurgical and Materials Transactions B*, 33(5):723–729.

Schei, A, Tuset, J K and Tveit, H, 1998. *Production of high silicon alloys*. (Tapir: Trondheim).

Tranell, G, Safarian, J and Wallin, M, 2020. SisAl - A New Process for Production of Silicon, in *Silicon for the Chemical and Solar Industry XV*, pp 129–139 (The Norwegian University of Science and Technology: Trondheim).

Yoshimura, H N, Abreu A P, Molisani A L, de Camargo A C, Portela J C S and Narita N E, 2008. Evaluation of aluminum dross waste as raw material for refractories, *Ceramics International*, 34(3):581–591.