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Effect of Copper, Zinc and Tin on the reaction between silicon and hydrogen chloride

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Abstract – Direct chlorination (DC) of metallurgical-grade silicon with anhydrous HCl is an industrial route to trichlorosilane (TCS), typically operated without intentional catalysts. In contrast, the methylchlorosilane direct synthesis (MCS) uses catalyst/promoter elements such as Cu, Zn and Sn, whose individual effects on silicon surface reactivity remain difficult to isolate because of CH_3Cl cracking and coke formation. In this work, DC was used as a simplified model system to evaluate the influence of typical MCS catalyst elements on TCS selectivity, reactivity and high-boiler formation. A synthetic silicon sample containing controlled amount of Fe, Al and Ca was tested with additions of Cu, Zn or Sn in a continuous lab-scale fluidized-bed reactor at 340 °C and 1.15 barg, with continuous silicon feeding to maintain a constant reaction mass. Product gases were analysed by online GC, and reacted residues were characterized by SEM–EDS. Cu increased silicon reactivity, lowering the reaction start temperature from 366 °C to 338 °C, without significantly affecting selectivity. Zn maintained high TCS selectivity but increased HCl loss, suggesting progressive surface deactivation through chloride-rich deposits. Sn had the strongest detrimental effect, decreasing TCS selectivity and preferentially increasing Si–Si bonded high boilers. SEM–EDS showed both Sn-rich particles and dispersed Sn in reacted Si-rich regions, indicating surface modification. These results identify Sn as a critical impurity for TCS production.

1. INTRODUCTION

1.1. Direct Synthesis

The Direct Synthesis (DS), also called the methylchlorosilanes synthesis (MCS), is a key step in silicone production. The direct process, discovered by Rochow-Müller in 1939, uses a copper-based catalyst for the reaction of Metallurgical grade silicon (MG-Si) powder with gaseous methyl chloride. Zinc (Zn), tin (Sn), and aluminum (Al) act as promoters to boost efficiency. Dimethyldichlorosilane ($(CH_3)_2SiCl_2$, M2), is the main product of the reaction but it is produced together with many by-products.

$$Si\ (s) + 2CH_3Cl\ (g) \rightarrow (CH_3)_2SiCl_2\ (g) \qquad (1)$$

Industrially this heterogeneous reaction takes place in a fluidized bed reactor under a pressure between 2.5 and 4 bars and a temperature around 300°C (Kanner & Lewis, 1993). Common objective of the MCS producers is to perform the reaction with a high productivity (50-80% of the methyl chloride consumed in the first pass), a high selectivity in M2 (more than 80% M2) and good silicon utilization (min 95% of the silicon converted to products).

Despite numerous studies and publications, today the mechanism of the direct synthesis of MCS has not been fully established. One challenge is that the direct synthesis suffers from a side-reaction where the CH_3Cl reagent cracks and forms carbonaceous compounds such as

CH_4 and solid carbon, which degrade the performance (Blaser et al., 2021). Formation of carbon compounds on the surface also makes it very difficult to characterize the reacting powder.

1.2. Direct Chlorination

The process to produce Trichlorosilane (TCS; $HSiCl_3$)) by reaction of Si and anhydrous HCl has been given several names. Direct chlorination (DC) has become a common name and is used in this paper. Alternate names for the reaction are low-pressure chlorination, direct TCS process and, to make things a bit confusing, hydrochlorination. But today, hydrochlorination is commonly used for the process to produce TCS by reaction of silicon, hydrogen and silicon tetrachloride (STC; $SiCl_4$). This process is not discussed in this paper.

TCS is the basis compound for semiconductor silicon (Ashworth, Bunge and Colomb, 2024) as well as silicon for photovoltaic applications and a wide range of materials known as organofunctional silanes.

In the direct chlorination process, hydrogen chloride gas fluidizes a bed of metallurgical grade silicon powder. TCS is produced at a high rate according to equation 2 and STC is formed in a consecutive reaction between TCS and HCl according to equation 3 and also according to equation 4A and 4B (Dropka et al., 2006).

$$Si\ (s) + 3HCl\ (g) \rightarrow HSiCl_3\ (g) + H_2\ (g) \quad (2)$$
$$HSiCl_3\ (g) + HCl\ (g) \rightarrow SiCl_4\ (g) + H_2\ (g) \quad (3)$$
$$Si\ (s) + 4HCl\ (g) \rightarrow SiCl_4\ (g) + 2H_2\ (g) \quad (4A)$$
$$HSiCl_3\ (g) + HCl\ (g) \rightarrow SiCl_4\ (g) + H_2\ (g) \quad (4B)$$

In addition to STC, the other typical by-products are dichlorosilane (DCS), and the so-called "high-boilers", which comprise several silanes compounds with Si-Si and Si-O-Si bonds.

Industrially this reaction takes place in a fluidized bed reactor under a pressure between 2 and 5 bars and a temperature between 300-400°C. The DC reaction is typically conducted in fluid bed reactors that contain a large internal heat exchanger to remove the high heat of reaction generated by the exothermic reaction. The DC process is typically operated without any catalysts since the impurities present in the metallurgical silicon are enough to ensure high HCl conversion.

Higher reaction temperatures favor higher STC yields and lower TCS yields. While not a topic of this paper, the DC reaction can be run in a fixed bed reactor with lumps of metallurgical grade silicon at ~1100°C-1200. (Crawford et al., 2022).

1.3. Industrial operation conditions

Table 1 : Comparison of Direct Chlorination and the Rochow-Müller reaction

	Direct Chlorination	**Direct Synthesis or Rochow-Müller Reaction**
Reactants	MG-Si + anhydrous HCl	MG-Si + methyl chloride CH_3Cl
Temperature[°C]	300-400	265-310
Pressure[bar]	2-5	2-4
Catalyst	No	Cu, Zn, Sn, P Different form
Target products	Trichlorosilane $HSiCl_3$	Dimethyldichlorosilane - $(CH_3)_2SiCl_2$
By-products	Silicon tetrachloride - $SiCl_4$ Dichlorosilane - SiH_2Cl_2 Several High Boilers (HB), primarily chlorinated disilanes, like hexachlorodisilane (Si_2Cl_6)	Methyltrichlorosilane – CH_3SiCl_3 – M1 Methyldichlorosilane - $(CH_3)SiCl_2$ – MH Trimethylchlorosilane – $(CH_3)_3SiCl$ – M3 Tetramethylsilane – $(CH_3)_4Si$ – M4 Several High Boilers (HB) $(CH3)_xSi2Cl_y$, (x+y = 6)

1.4. Why this study

Direct synthesis is more complex than direct chlorination because it involves interactions among catalysts and promoters such as Cu, Zn, Sn, and other elements. In addition, methyl chloride introduces carbon into the system. During direct synthesis, CH_3Cl can crack in a side reaction, forming H_2, HCl, CH_4, and solid and liquid hydrocarbons (Blaser et al., 2021). These hydrocarbons, commonly referred to as coke, may deposit on active sites, lowering the productivity of $(CH_3)_2SiCl_2$, and lead to deactivation. (Blaser et al., 2021). CH_3Cl cracking also results in production of higher levels of lower value compounds such as methyldichlorosilane [MH; CH_3SiCl_2H] and methyltrichlorosilane [M1; CH_3SiCl_3].

In MCS chemistry, Zn and Sn are also known as important promoter elements, which have long been used to influence catalyst performance and product selectivity in the Rochow-Müller reaction. Although their beneficial effects have been widely recognized, their mechanistic roles remain not fully understood. Previous studies suggest that these elements can modify the electronic structure and adsorption behavior at active silicon surface sites, thereby affecting the dissociation of reactant molecules and subsequent surface reactions (Tanaka et al., 2003). In particular, Zn and Sn have been reported to exhibit distinct adsorption characteristics on Si surfaces, implying potentially different impacts on catalytic activity and by-product formation.

In addition, Cu and Zn may be present as trace elements in silicon raw materials. Tveit and Myrhaug (2000) describe that electrodes could contain some copper and biocarbon (charcoal and woodchips) could contain some zinc. Lindstad and Forseth (2024) show that the origin of the raw material for pyrolysis to make biocarbon will influence the trace element content in the silicon, especially the zinc. Switching from fossil carbon (coal, coke) to biocarbon (charcoal, woodchips) is a major lever for silicon producers to decrease their emissions (Ausland and Rong, 2020).

The recycling of crystalline silicon photovoltaic modules inherently reintroduces metallic impurities originally present in the panel structure, including Cu and Sn (Chen *et al*., 2024). These elements are integral to solar panel components and are quantitatively identified within the silicon cell fraction of the module composition (Chen *et al*., 2024). During recycling processes these metals may be recovered together with silicon, thereby creating a pathway for Cu and Sn contamination in recycled silicon feedstock (Chen *et al*., 2024).

This study, therefore, investigates whether typical MCS catalyst elements influence DC performance and how these catalysts deposit on the silicon surface.

2. EXPERIMENTAL SECTION

A series of laboratory experiments was conducted on a laboratory reactor to evaluate the effect of MCS catalysts (Cu, Zn, and Sn) on DC performance, including TCS selectivity, reactivity, and by-product formation. The study also aimed to investigate the distribution of the different catalysts on the silicon surface. This is why SEM-EDS analyses were performed to examine how the catalysts were deposited on the silicon after the reaction.
These experimental results are presented in this section.

2.1. Sample preparation

Five experiments were run in the lab scale DC reactor. The Al, Ca and Fe have been measured while the Cu, Zn and Sn have been calculated.

Table 2 : Composition of Samples with trace metal additions

Experiment	Al (weight %)	Ca (weight %)	Fe (weight %)	Cu (weight ppm)	Zn (weight ppm)	Sn (weight ppm)
Si-Fe-Al-Ca	0,11	0,006	0,27	-	-	
Si-Fe-Al-Ca 1000 ppm Sn	0,11	0,006	0,27	-	-	1 000
Si-Fe-Al-Ca 100 ppm Sn	0,11	0,006	0,27	-	-	100
Si-Fe-Al-Ca 1000 ppm Cu	0,11	0,006	0,27	1 000	-	-
Si-Fe-Al-Ca 1000 ppm Zn	0,11	0,006	0,27	-	1 000	-

The Si-Fe-Al-Ca sample has been made from pure silicon (polysilicon supplied by Wacker Chemie GmbH) melted and alloyed with iron (Fe), aluminum (Al) and calcium (Ca) in Elkem laboratory in Kristiansand (Norway). The level of Fe, Al and Ca has been decided to be close to typical value for MG-Si and pure silicon was used as a starting material to avoid any impact of other trace elements that can be found in MG-Si.
The tin was used as powder metallic form from Alfa Aesar®, with a top size of maximum 150 µm and purity of 99,995 % on metal basis.
The zinc was used as a powder metallic form from Alfa Aesar® with a top size of maximum 150 µm and a purity of 99,9%.
The Cu catalyst is added as a master alloy made from high purity Si and Cu. This master alloy is mixed with the Si sample to get the desired level of Cu, the fraction 125-180 µm used during the experiment had a content of 3,2 % Cu measured by XRF.

2.2. Lab-scale fluidized-bed DC reactor

The five experiments were run under identical reaction conditions described above. Experiments were conducted in a continuous laboratory-scale fluidized-bed DC reactor

operated at 1.15 barg and 340 °C. Silicon samples with very low reactivity will not react at 340 °C and need higher temperature (360 °C) to complete the experiment. The energy produced by reacting the HCl is important in maintaining the reaction rate. If the reaction stops it is typical that the reaction has to be restarted at a higher temperature.
Ground silicon was continuously added to maintain 5 g of reaction mass, using a particle size range of 125–250 µm. A continuous feed of anhydrous HCl with a small amount of argon was supplied to the reactor, with argon serving as an internal standard for the online gas chromatograph (GC). A filter positioned outside the reactor captured entrained fines and removed some impurities during operation. The process gas was then automatically analyzed by the online GC.
TCS selectivity is defined as the molar percentage of TCS in the product stream relative to the total chlorosilanes produced (TCS, STC, DCS, and high boilers). It is reported on a hydrogen-free and HCl-free basis. DCS and high-boiler selectivity are calculated in the same way. High boilers are defined in Table 3.
HCl loss is defined as the fraction of HCl that is not converted in the reactor, determined by measuring the residual HCl concentration in the reactor off-gas (Hesse and Pätzold, 2006). In a highly reactive system, most of the supplied HCl is consumed, and the residual HCl concentration may therefore fall below the gas chromatograph (GC) detection limit. Conversely, in a system with low reactivity, a larger fraction of HCl remains unreacted and can be detected by GC. HCl loss is used as an inverse indicator of silicon reactivity: low HCl loss indicates high reactivity, whereas high HCl loss indicates low reactivity.
The main performance indicators were total silicon consumption (up to 70 g, 12 reactor volumes), TCS selectivity, HCl loss (or reactivity), DCS selectivity, and high-boiler selectivity.

2.3. Gas chromatograph measurements

All selectivity measurements and the other quantified gas analyses are produced by a Varian 3900 gas chromatograph (GC). The GC is equipped with a packed column (30% QF1, 80/100 Chromosorb PAW) and a thermal conductivity detector (TCD). The product gas is sampled about each 19 minutes.

It was previously shown that by selecting appropriate chromatographic columns and optimizing the sample amount, various high-boiling components were successfully detected and quantified (Hoel and Rong, 2020). At present, the five types of high boilers given in Table 3 can be identified. Of the five compounds, three are siloxane species (HB1, HB2 and HB3) containing Si–O–Si linkages, while the remaining two (HB4 and HB5) are high-boiling species with Si–Si bonds:

Table 3 : list of High Boiler observed

HB	Formula	Likely name
HB1	$SiHCl_2$-O-$SiHCl_2$	Tetrachlorodisiloxane
HB2	$SiCl_3$-O-$SiHCl_2$	Pentachlorodisiloxane
HB3	$SiCl_3$-O- $SiCl_3$	Hexachlorodisiloxane
HB4	Cl_3Si-$SiHCl_2$	Pentachlorodisilane
HB5	Cl_3Si-$SiCl_3$	Hexachlorodisilane

2.4. SEM-EDS characterization of reaction residues

The solid residues obtained from the reactor after the reaction were characterized by scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS). The samples were mounted on aluminum stubs without further treatment.

SEM observations were carried out in backscattered electron (BSE) mode at an accelerating voltage (EHT) of 15 kV to examine the morphology and microstructure of the residues.
In addition, elemental distribution was evaluated by EDS mapping to visualize the spatial distribution of Si, Fe, Al, Ca, Cu, Zn and Sn in the samples.
Figure 1 presents representative SEM images of unreacted silicon particles with an initial size of 125–250 µm (a) and reacted particles collected after the experiment (b), showing consumed regions and crater-like reaction sites.

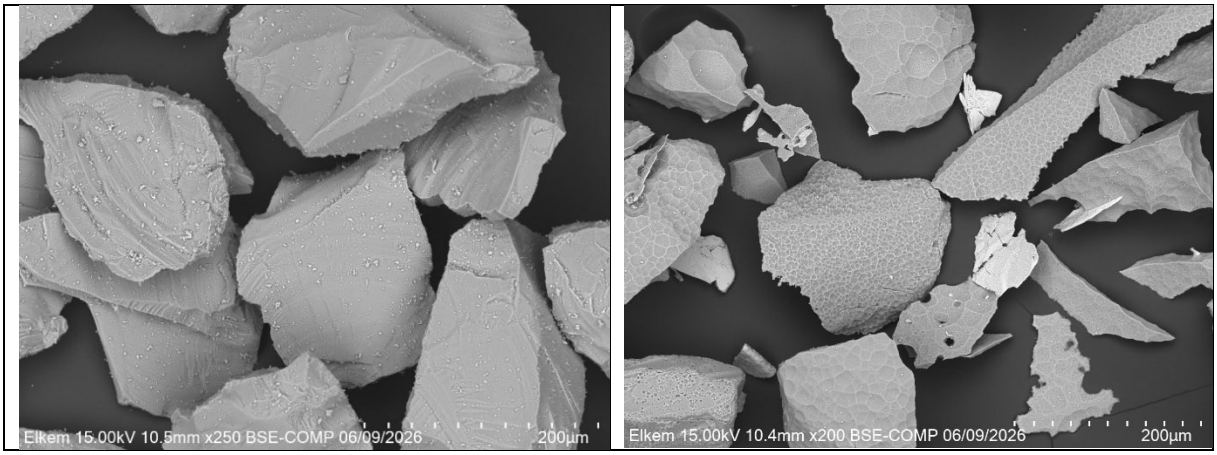


Figure 1: Unreacted silicon at 250x (a) and reacted silicon at 200x (b)

3. RESULT and DISCUSSIONS

3.1. Impact of Copper

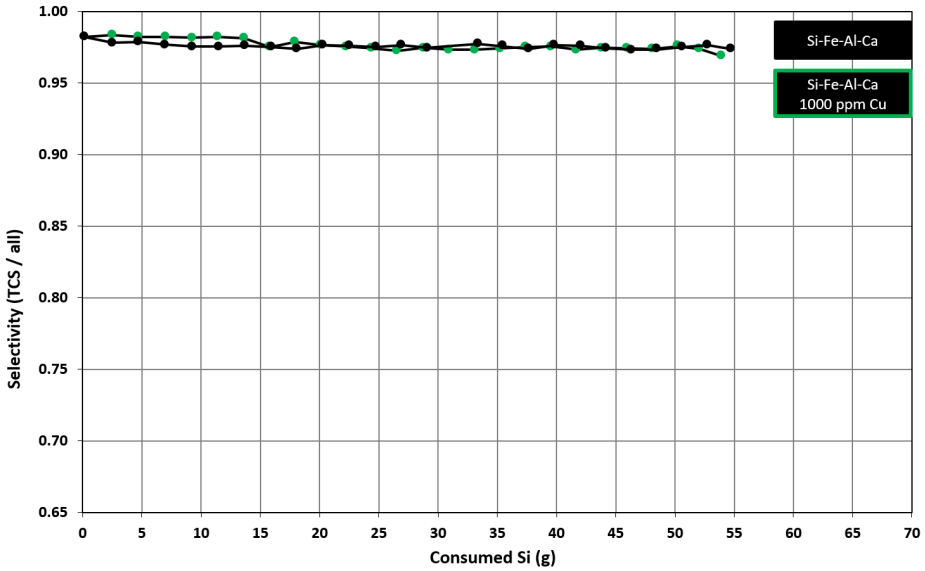


Figure 2 : Evolution of the TCS selectivity for reference sample and sample with 1000 ppm Cu

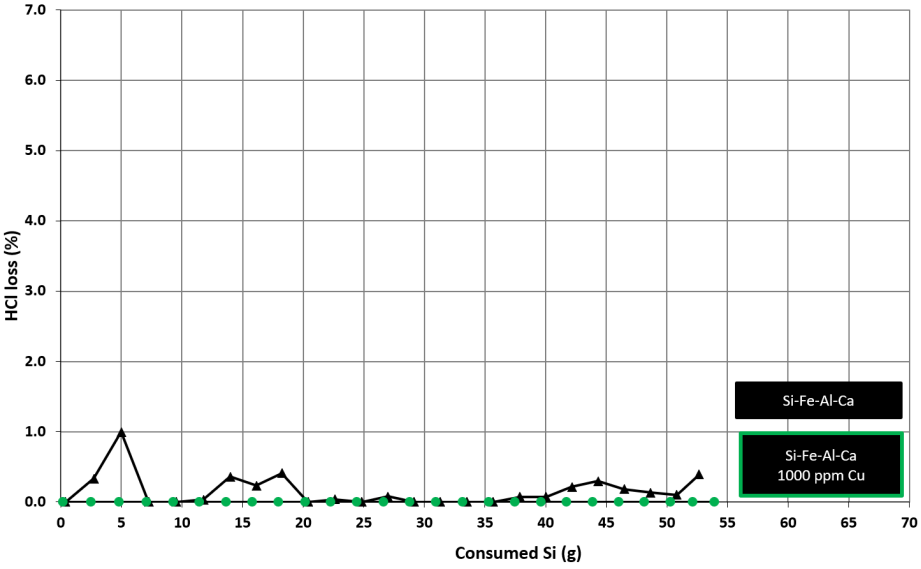


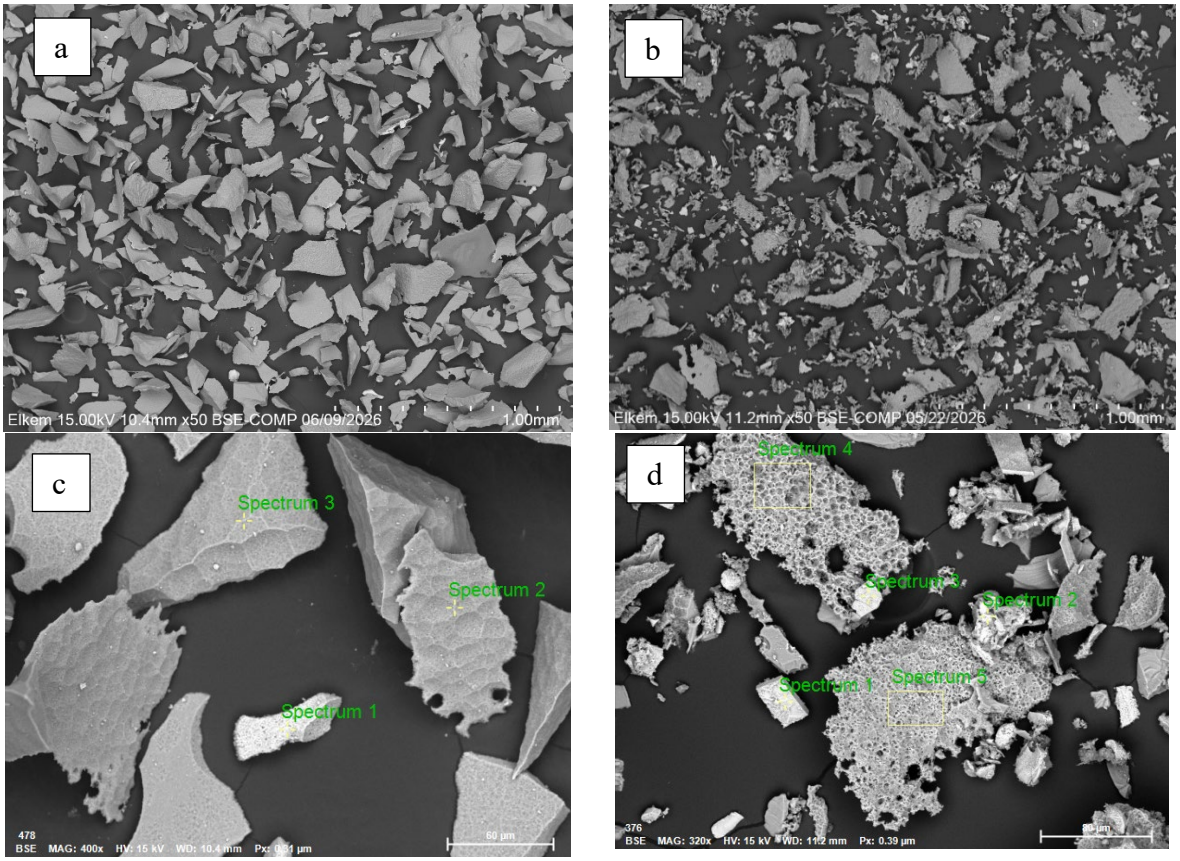
Figure 3 : Evolution of the HCl loss (%) for reference sample and sample with 1000 ppm Cu

The TCS selectivity of the reference material and the experiment with copper is shown in Figure 2. It should be noted that the reference material gives a TCS selectivity of about 97% and compared to typical MG-Si material this is a very high TCS selectivity and therefore it is the trace elements that are not present in the reference material that is impacting the TCS selectivity. There is no significant difference in TCS selectivity for the two experiments. The HCl loss is shown in Figure 3.

The experiment with 1000 ppm Cu shows no HCl loss, indicating high reactivity. This catalytic effect is also reflected in the reaction onset temperature, defined as the reactor-wall temperature required to initiate direct chlorination. In fact, each reaction is initially started by charging 5 grams of silicon to the reactor, starting gas (HCl + argon) feed and gradually increasing the reactor temperature to 380 °C by applying heat to the reactor. When the reaction starts, observed by a decrease in the reactor overhead pressure, the temperature controller is placed in automatic at a setpoint of 340 °C. The reaction onset temperature is the temperature when the pressure decreases.

The reference sample starts reacting at 366 °C, whereas the sample with 1000 ppm Cu starts at 338 °C, corresponding to a 28 °C decrease. In addition, *Figure 4* shows clear differences in reactor residue morphology. The Cu-containing residue (b and d) appears more fragmented, with more fine debris and disrupted particles. This may indicate that freshly added silicon requires time to react in the reference system, whereas in the presence of Cu the reaction proceeds faster and consumes the newly added particles. Ehrich et al. (1998) demonstrate that the silicon reactivity dramatically increases in presence of copper.

No significant differences are observed on TCS selectivity or DCS and High boiler formation. Cu is mainly impacting the reactivity.



e

Atomic concentration /%

Spectrum	O	Al	Si	Cl	Ca	Fe	Pt
Spectrum 1	16.77	13.55	43.06	1.18	0.47	24.97	0.00
Spectrum 2	13.51	0.46	83.89	0.99		1.14	0.00
Spectrum 3	7.77		91.18	0.35		0.69	0.00

f

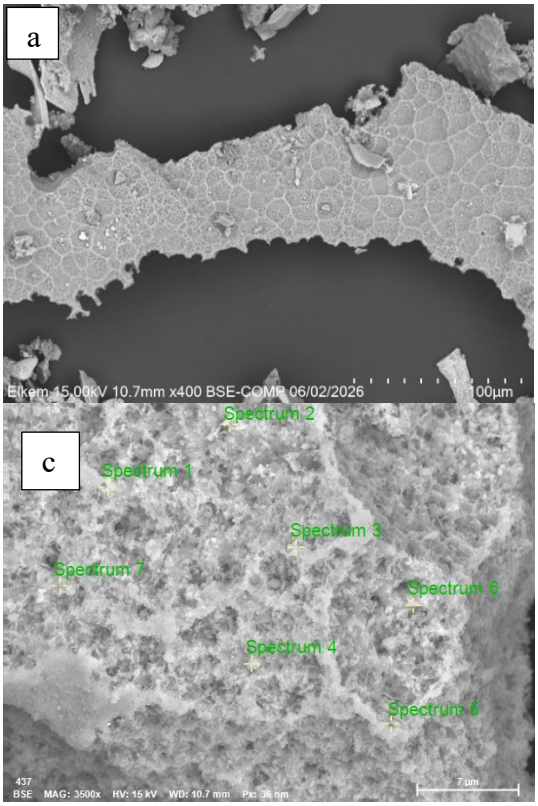
Atomic concentration /%

Spectrum	O	Al	Si	Cl	Ca	Fe	Cu	Pt
Spectrum 1	33.50	8.48	32.90	3.32	1.20	20.17	0.43	0.00
Spectrum 2	30.59	1.19	17.39	33.58		4.62	12.62	0.00
Spectrum 3	6.67	33.22	35.10	0.57		24.43		0.00
Spectrum 4	17.47	0.71	79.49	0.95		1.39		0.00
Spectrum 5	10.84	0.50	84.66	1.78		1.29	0.93	0.00

Figure 4 : Reacted silicon particles from reference sample (a at 50x and c at 400x) and from sample with 1000 ppm Cu (b at 50x and dat 320x) and semi quantitative composition of spectrum for reference sample (e) and sample with 1000 ppm Cu (f)

The SEM analysis of the experiment performed with 1000 ppm of Cu shows a homogeneous distribution of Cu across the silicon surface (c and d, *Figure 5*)). The silicon particles appear to be significantly consumed over most of the surface (a, *Figure 5*). Small craters can be observed, corresponding to areas where silicon has been locally consumed (b, *Figure 5*). Inside these craters (c, *Figure 5*), a porous structure with small holes is visible, suggesting localized material consumption.

The semi-quantitative EDS analysis (d, *Figure 5*) indicates that silicon is the dominant element in all analyzed areas (>85 at.%), with minor amounts of O, Fe, Al, Cl, and Cu. Oxygen is found due to oxidation of the surface after removing from the reactor. Copper is detected in all spectra at low concentration and appears to be homogeneously distributed.



d

Atomic concentration /%

Spectrum	O	Al	Si	Cl	Ca	Fe	Cu	Pt
Spectrum 1	18.57	0.63	77.59	1.16	0.16	1.44	0.45	0.00
Spectrum 2	16.80	0.73	79.18	1.29		1.53	0.47	0.00
Spectrum 3	11.01	0.66	86.34	0.95		0.75	0.29	0.00
Spectrum 4	14.53	0.70	81.71	1.15		1.34	0.58	0.00
Spectrum 5	19.55	1.02	74.97	2.01		1.40	1.04	0.00
Spectrum 6	19.54	0.82	75.90	1.68	0.08	1.47	0.51	0.00
Spectrum 7	8.20	0.58	89.57	0.67		0.55	0.43	0.00

Figure 5 : Reacted silicon particles form sample with 1000 ppm Cu at 400x (a), 2300x µm (b), 3500x (c) and semi quantitative composition of spectrum (d)

3.2. Impact of Zinc

The impact of Zn addition on both TCS selectivity and reactivity was evaluated by comparing a reference sample with a sample containing 1000 ppm Zn.
As shown in *Figure 6*, the experiment with Zn gives slightly higher TCS selectivity than the reference.

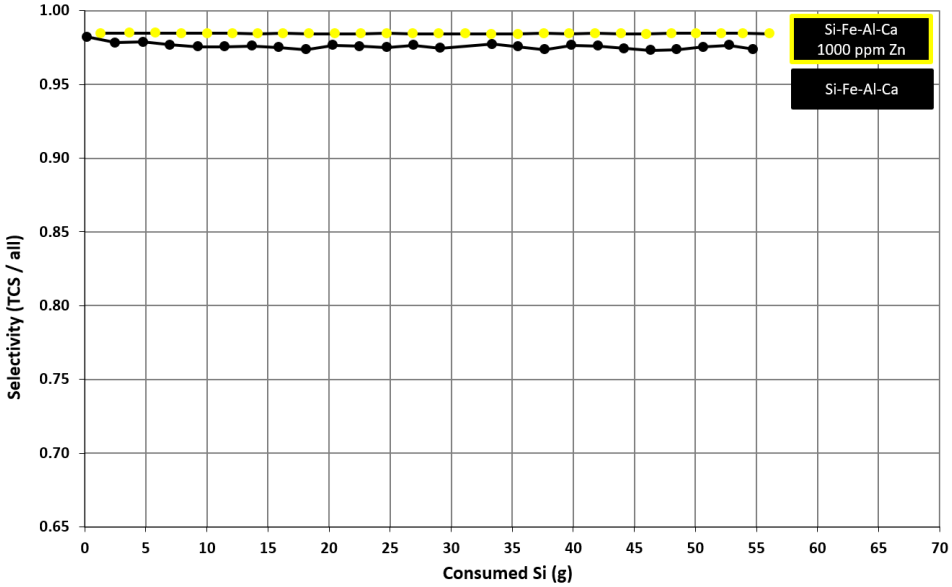


Figure 6 : Evolution of the TCS selectivity for reference sample and sample with 1000 ppm Zn

Figure 7 shows a significant increase in HCl loss in the presence of Zn, particularly at higher silicon conversion levels, where values exceed 5–6%, whereas the reference sample remains close to zero.
These results suggest that Zn does not affect the selectivity toward TCS formation, but a lower reactivity demonstrated by an increasing fraction of unreacted HCl over time compared to the reference system.

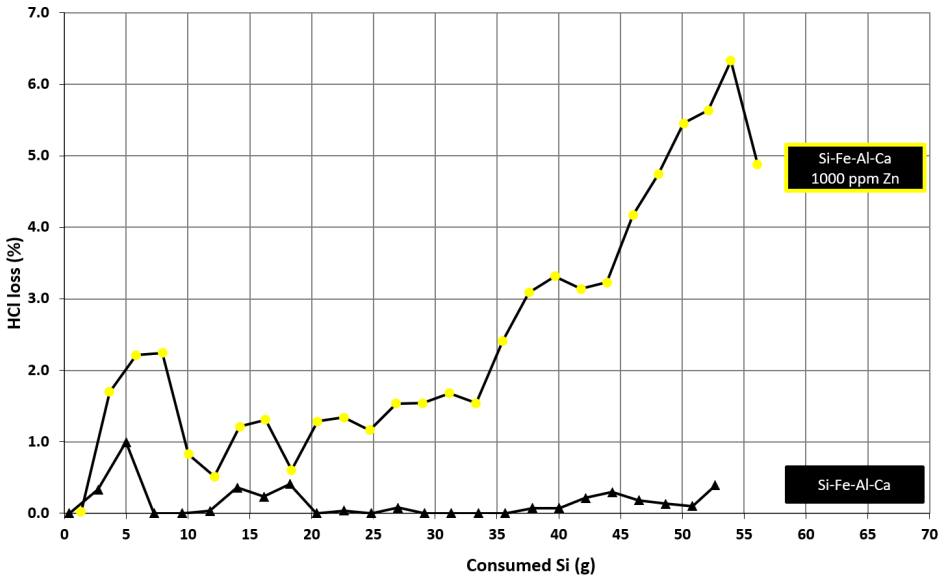
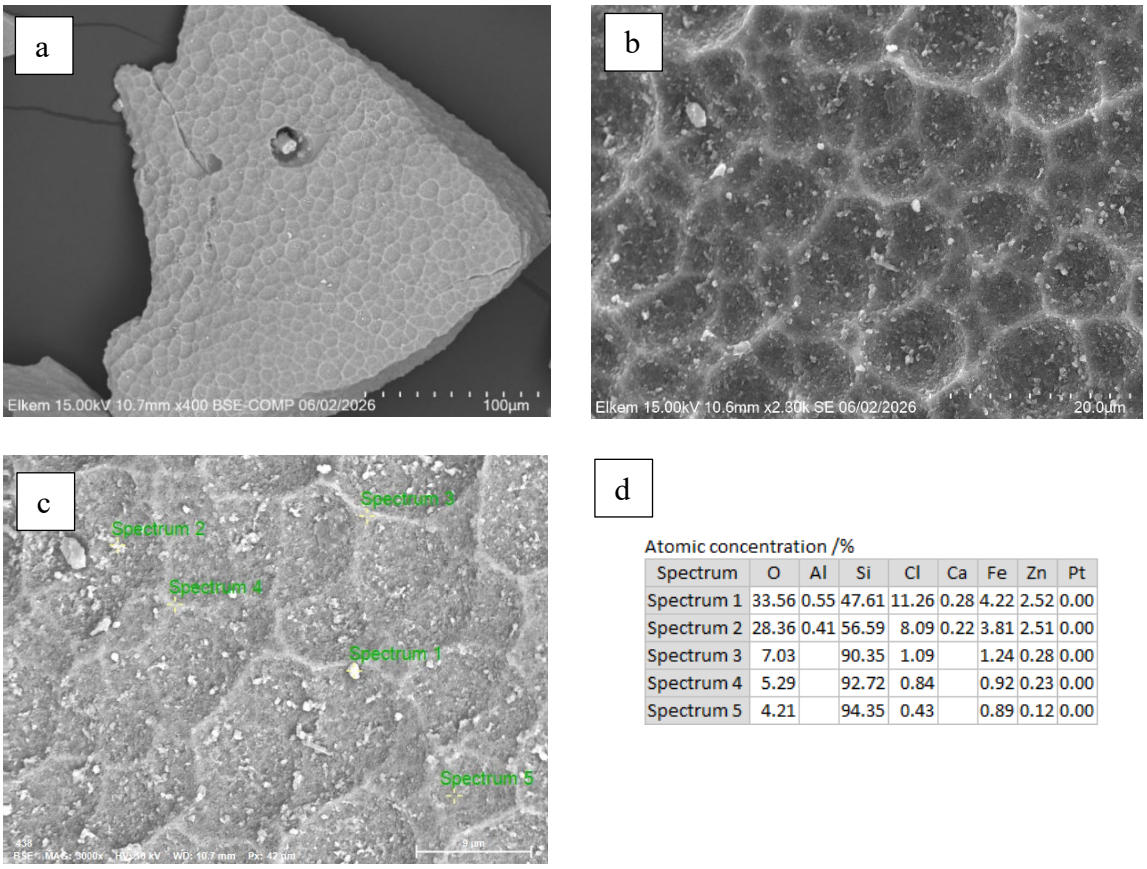


Figure 7 : Evolution of the HCl loss (%) for reference sample and sample with 1000 ppm Zn

Very small white deposits can be observed on the surface, *Figure 8* a, b and c. These deposits correspond to spectra 1 and 2 (*Figure 8* (d)) and contain Zn, Fe and Cl. They likely originate from a Zn–Fe chloride-derived phase. Over time, this phase could accumulate and limit access to Si surface.
Spectra 3, 4 and 5 correspond to the Si-rich matrix (>90 at.% Si), which represents the primary reaction surface. The presence of residual Zn in these regions suggests partial incorporation or surface interaction of Zn species within the active silicon phase.



Atomic concentration /%

Spectrum	O	Al	Si	Cl	Ca	Fe	Zn	Pt
Spectrum 1	33.56	0.55	47.61	11.26	0.28	4.22	2.52	0.00
Spectrum 2	28.36	0.41	56.59	8.09	0.22	3.81	2.51	0.00
Spectrum 3	7.03		90.35	1.09		1.24	0.28	0.00
Spectrum 4	5.29		92.72	0.84		0.92	0.23	0.00
Spectrum 5	4.21		94.35	0.43		0.89	0.12	0.00

Figure 8 : Reacted silicon particles from sample with 1000 ppm Zn at 100 µm (a), 20 µm (b), 7 µm (c) and semi quantitative composition of spectrum (d)

3.3. Impact of tin

It was found that tin, tested at two different levels, has a large negative impact on TCS selectivity, (*Figure 9*). The experiment with 1000 ppm Sn in the feed gave a very strong negative effect on TCS selectivity and at the end of the experiment the TCS selectivity was only about 70%. Originally, the plan was to only run experiments with 1000 ppm Cu, Zn or Sn in the feed, but due to the very strong effect of Sn it was decided to run a new experiment with 100 ppm Sn in the feed.

The sample containing 1000 ppm Sn showed approximately 10% lower TCS selectivity than that containing 100 ppm Sn (*Figure 9*). This trend suggests that the detrimental effect of Sn addition on selectivity becomes increasingly significant with higher Sn content. While the reference sample maintains a high and stable TCS selectivity at 98%, the addition of 100 ppm Sn leads to a noticeable decline to approximately 85%, and further addition to 1000 ppm results in an even lower selectivity in the range of 70%.

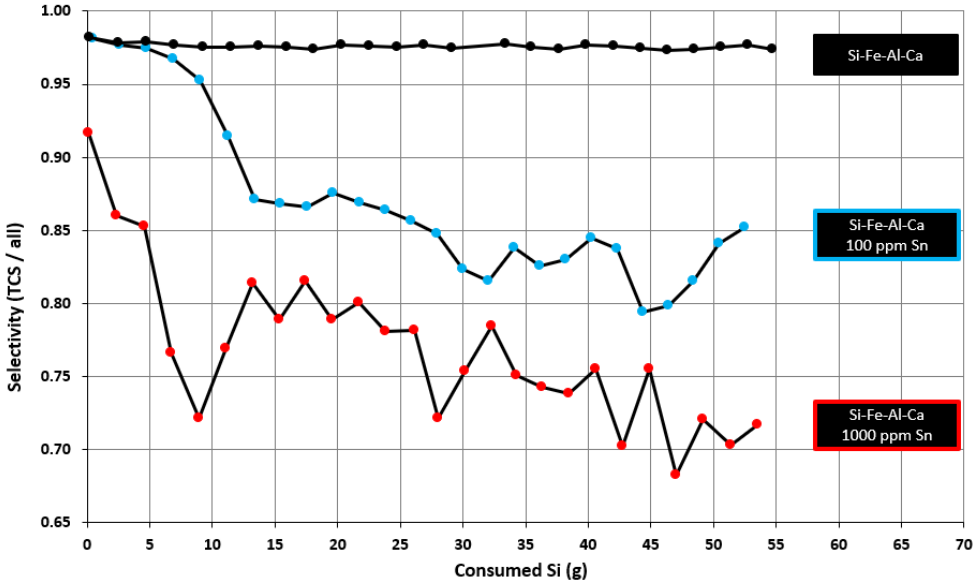


Figure 9 : Evolution of the TCS selectivity for reference sample, sample with 1000 ppm Sn and sample with 100 ppm

In addition, Figure 10 shows that HCl loss is strongly affected by Sn addition. The reference sample exhibits negligible HCl loss, whereas the 100 ppm Sn sample shows a substantial increase, reaching up to ~5%, and the 1000 ppm Sn sample maintains elevated values around ~1–2%.

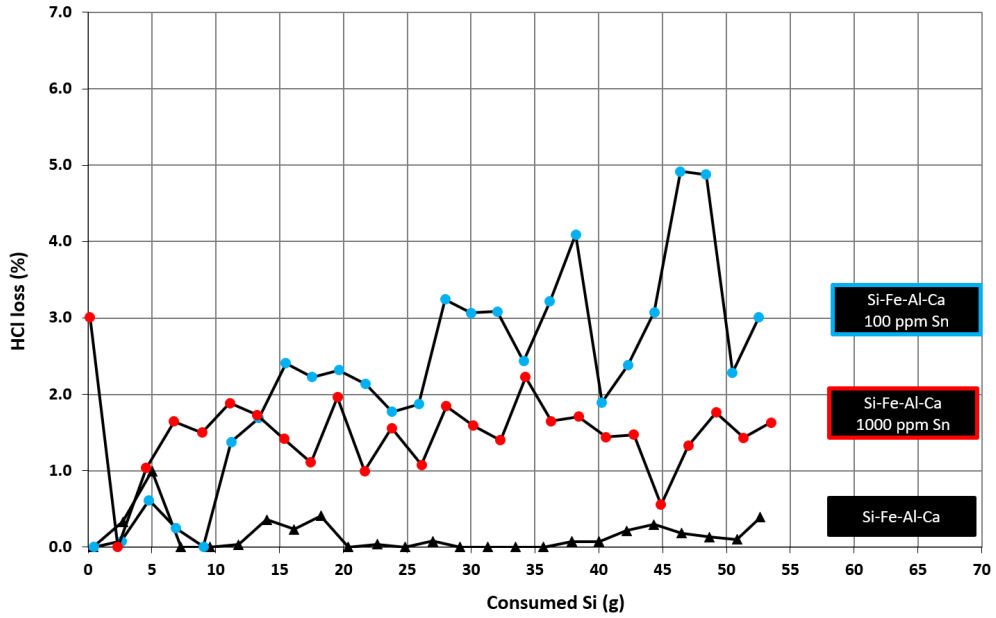
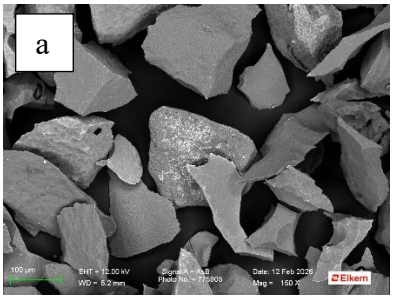
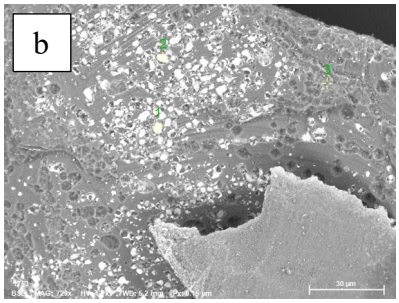


Figure 10 : Evolution of the HCl loss (%) for reference sample, sample with 1000 ppm Sn and sample with 100 ppm

The SEM observations first reveal the presence of numerous white particles distributed on the silicon surface (*Figure 11*), corresponding to Sn-rich regions. EDS analysis (*Figure 11*) confirms that these particles contain a high concentration of Sn, indicating a strong accumulation of Sn in some areas.





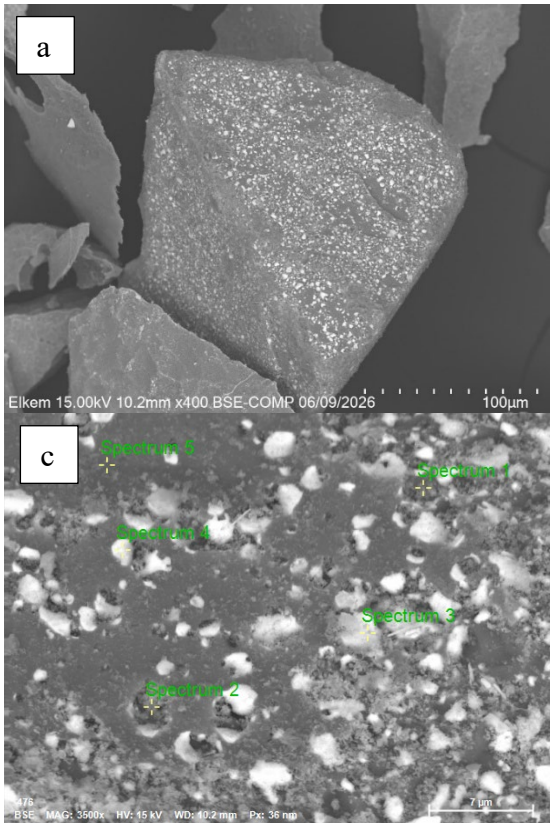
c

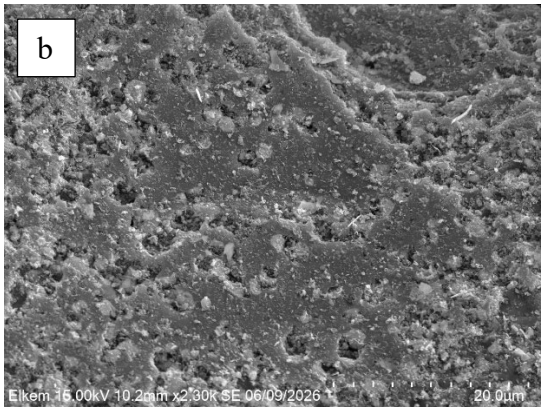
Atomic concentration /%

Spectrum	O	Si	Cl	Cr	Fe	Sn	Au
1	27.7	29.6	0.8		1.0	40.8	0.0
2	12.4	26.3		2.0	9.9	49.3	0.0
3	2.7	95.3			2.0		0.0

Figure 11 : Reacted silicon particles form sample with 1000 ppm Sn at 100 µm (a), 30 µm (b), and semi quantitative composition of spectrum (c)

At higher magnification, the silicon surface appears heterogeneous (c *Figure 12*), with the presence of crater-like regions associated with silicon consumption and regions with "white deposit". These crater areas do not necessarily contain visible Sn-rich particles (spectrum 1, 2 and 5 d *Figure 12*). EDS analysis performed in these regions shows that Sn is still systematically present on the silicon surface, with typical concentrations in the range of 1–5 %.
This demonstrates that Sn is not only present as "white deposit" but is also distributed within the reacted silicon regions. Two distinct types of Sn-containing domains can therefore be identified: (i) localized region with high Sn content, and (ii) Si-rich regions containing a lower amount of Sn (d *Figure 12*).





d

Atomic concentration /%

Spectrum	O	Si	Cl	Cr	Fe	Sn	Pt
Spectrum 1	11.36	84.50	0.87		0.38	2.89	0.00
Spectrum 2	20.18	71.97	1.71		2.73	3.41	0.00
Spectrum 3	15.19	40.27	0.88	1.13	11.72	30.81	0.00
Spectrum 4	16.31	43.47	0.88	1.43	9.57	28.35	0.00
Spectrum 5	6.62	90.70	0.30		0.36	2.03	0.00

Figure 12 : Reacted silicon particles form sample with 1000 ppm Sn at 100 µm (a), 20 µm (b), 7 µm (c) and semi quantitative composition of spectrum (d)

The influence of Sn on the formation of high-boiling (HB) components was further analyzed by monitoring the evolution of individual HB species, which were quantified by gas chromatography (GC).
As shown in *Figure 13*, the formation of HB1 and HB3 (siloxane species containing Si–O–Si linkages) remains relatively low and exhibits only a weak dependence on Sn concentration. The amount of oxygen containing high boilers is limited by the availability of oxygen (mainly surface oxygen introduced with the silicon powder). Although a slight increase can be observed for the Sn-containing samples, the overall contribution of these oxygen-bridged species is limited.

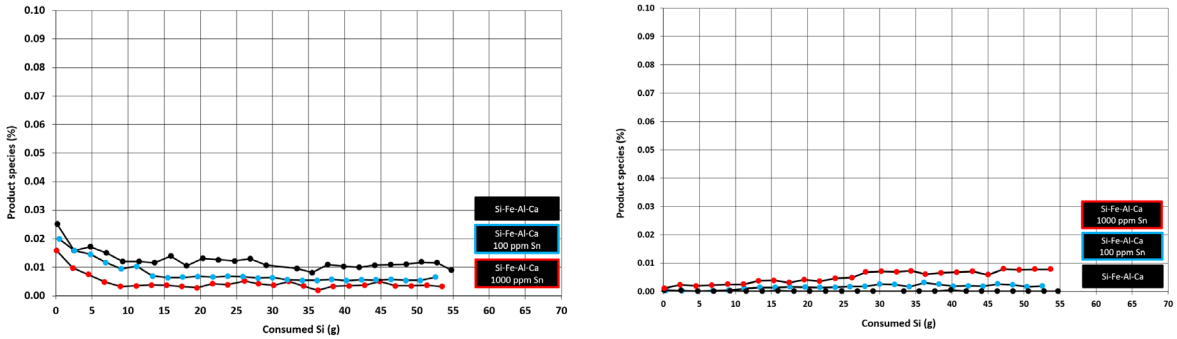


Figure 13 : Evolution of the HB1(left) and HB 3(right) for reference sample, sample with 1000 ppm Sn and sample with 100 ppm

In contrast, *Figure 14* reveals a pronounced increase in HB4 and HB5, which correspond to Si–Si bonded high-boiling species. This increase is particularly significant for the sample containing 1000 ppm Sn, where both HB4 and HB5 rise sharply with increasing silicon consumption and Sn accumulation, reaching substantially higher levels than those observed for the reference and 100 ppm Sn samples. For the sample containing 100 ppm Sn, the impact is mainly on HB5. These results indicate that Sn promotes the formation of Si–Si bonded high-boiling species.

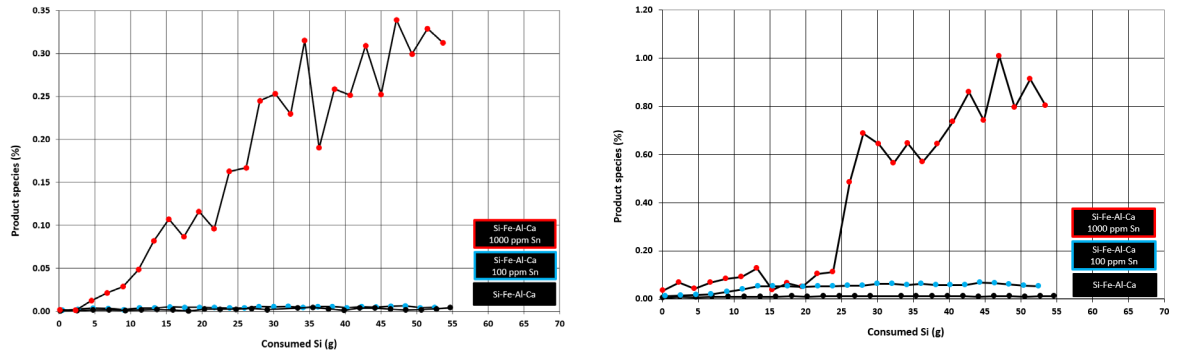


Figure 14 : Evolution of the HB4(left) and HB 5(right) for reference sample, sample with 1000 ppm Sn and sample with 100 ppm

In summary the Sn-containing experiment exhibits a significant increase in the formation of high-boiling species, particularly Si–Si bonded compounds, together with a lower TCS selectivity and incomplete HCl conversion.
This behavior can be correlated with the surface structure revealed by SEM–EDS, which shows that Sn is present in high concentration level and as a dispersed phase on the silicon surface. The industrial relevance of the observed Sn effect is particularly important when considering

high-boiling residue formation in TCS production. High boilers are undesirable because they represent both a loss of valuable chlorosilanes and an additional downstream treatment burden. In industrial direct chlorination, the production of trichlorosilane generates significant volumes of by-products with boiling points above 100 °C (boiling point of Hexachlorodisilane (HB 5) is 144 °C), predominantly disilanes and disiloxanes. These residues have traditionally been removed from the product stream together with silicon fines and aluminum chloride solids and disposed of as slurry, leading to losses of valuable TCS and STC in the waste stream (Kroupa, 2002). In the present study, Sn addition strongly decreased TCS selectivity and preferentially increased the formation of Si–Si bonded high-boiling species, especially HB4 and HB5. This indicates that Sn contamination may not only reduce the yield of the desired TCS product but also increase the load on downstream high-boiler recovery, residue treatment and waste-management systems. From an industrial perspective, Sn should therefore be considered a critical impurity in silicon feedstocks for direct chlorination.

3.4. Proposed role of Sn in promoting Si–Si bond formation during direct chlorination

Sn present on the reacting silicon surface may first modify the local active sites. This can occur by interaction with exposed silicon atoms, by formation of small Sn aggregates, or by possible partial incorporation of Sn into the near-surface region. This interpretation is consistent with surface-science studies of Zn and Sn on clean Si(111)-7×7 (Tanaka et al., 2003). These observations suggest that Sn can locally change the structure of the silicon surface.

The possible role of Sn in forming Si–Si bonded species is also supported by the work of Shimada, Nagashima and Aramata (2006). They studied Sn-containing contact masses for phenylchlorosilane synthesis and observed white precipitates on silicon wafer surfaces when Sn was present. These precipitates were identified as chlorine-rich branched polysilanes. The authors proposed that reactive silylene-like species formed on the silicon surface and contributed to the formation of these precipitates. Their system was based on chlorobenzene and not HCl, but it gives a useful analogy. It suggests that Sn can favor the formation of silylene-like species on silicon surfaces, which may then lead to Si–Si coupling.

The Photo-EMF study of Lorey et al. (2000) gives another indication that Sn may affect silicon reactivity through electronic effects. In this work, the electronic state of the silicon was shown to influence both selectivity and the amount of disilanes in the crude silane mixture. A higher Sn concentration relative to phosphorus was associated with p-type Photo-EMF behavior, while a higher P/Sn ratio shifted the silicon toward stronger n-type behavior. This study was performed for organohalosilane direct synthesis and not for HCl direct chlorination. However, it supports the general idea that Sn can change the electronic character of reactive silicon surfaces and impact disilane formation.

In the present direct chlorination system, Sn-modified areas may therefore favor the formation of silylene-like species during the reaction with HCl. If these intermediates couple together, they can form new Si–Si bonds. This gives a possible explanation for the increased formation of Si–Si-containing high boilers observed in the Sn-containing samples.

Crawford et al (2022) showed that Germanium (Ge) had a strong impact on TCS selectivity. Although Ge and Sn may act through different mechanisms, the reported effect of trace Ge on direct chlorination supports the broader hypothesis that Group 14 impurities can strongly influence silicon surface reactivity and selectivity. Lead (Pb), known as dangerous inhibitor in the direct process, could also be a good candidate for a similar study.

4. CONCLUSION

Beyond the direct effect of Cu, Zn, and Sn on DC performance, this work demonstrates the value of combining controlled laboratory-scale reaction testing with SEM–EDS characterization of reactor residue. Laboratory reactor data provide quantitative information on reactivity, TCS selectivity and high-boiler formation, while SEM–EDS reveals how the added elements are distributed on the reacted silicon particles. This combined methodology makes it possible to make the link between lab results and visual observation at silicon surface level.

Direct chlorination was used as a simplified model system to study MCS catalyst elements without the additional complexity of CH_3Cl cracking and coke formation. This allowed the intrinsic effect of Cu, Zn, and Sn on the silicon surface to be evaluated more directly. One learning for MCS is that high level of Sn could probably increase Si–Si bonded high-boiler formation.

Industrially, the most important finding is that Sn is a critical impurity for direct chlorination. Even at low concentration, it decreases TCS selectivity and promotes Si–Si bonded high boilers, increasing product losses and residue-management challenges. Zn is less harmful to selectivity, but it may reduce reactivity over time through chloride-derived surface deposits.

These findings have significant implications for future silicon feedstocks, notably recycled silicon recovered from end-of-life solar modules, potentially containing residual tin from solder materials, and biocarbon-based silicon, for which Sn and Zn concentrations may vary according to the origin and composition of the biocarbon feedstock.

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