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Corrosion of Superalloys typically used as reactor material for the reaction between Si, $SiCl_4$ and H_2.

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Abstract – Superalloys, like for instance Incoloy®800H (UNS N08810), are the preferred construction material in hydrochlorination reactors due to their excellent thermal and chemical stability. These alloys typically contain a high amount of nickel and chromium.
Some of the alloy components will react with the silicon compounds in the hydrochlorination process (for instance $HSiCl_3$) to form silicides on the reactor wall. The silicides will easily oxidize if oxygen and water gets into the reactor, for instance during maintenance or turnaround of the reactor. Some of the oxygen will remain on the reactor wall after restart, and give a permanent reduction in the $HSiCl_3$ selectivity. Silicide formation, and subsequent loss when the reactor is opened for planned and unplanned maintenance, is the main source of internal surface corrosion that ultimately determines the operational life of the very expensive reactor vessel.
The formation of silicide on the superalloy reactor wall is demonstrated with small scale reactors followed by characterization with scanning electron microscope.

1. INTRODUCTION

Elkem is a producer of metallurgical silicon for several applications. To understand and optimize the performance of our silicon, we often develop laboratory test equipment to simulate the performance in the customer processes. Back in 2004 we started to evaluate the performance of silicon in the reaction between silicon, silicon tetrachloride (STC), and hydrogen for the production of trichlorosilane (TCS). See equation 1. This process is often called the HC process, but is also referred to as the hydrogenation process or the dirty recycle process.

$$Si\ (s) + 3SiCl_4\ (g) + 2H_2\ (g) \leftrightarrow 4HSiCl_3\ (g) \qquad (1)$$

Trichlorosilane is the precursor for production of semiconductor and photovoltaic grade of silicon. The advantage with the HC process is that all STC produced in the chemical vapor decomposition step (CVD) can be recycled back to TCS. It is also common to return the HCl produced in the CVD process to the HC process and in more recent years to also use anhydrous HCl as the source of makeup chlorine for the plant instead of purchased STC. None of the original HC industrialization by Union Carbide, including extensive corrosion studies, considered co-feed of any amount of anhydrous HCl – only the system Si, H_2 and STC. The TCS selectivity in the HC process is typically about 25 mole % and therefore the STC must be passed about 4 times though the HC process to be completely consumed. In practical terms, unreacted STC will be recovered from the product gas, mixed with STC from the CVD process and returned (with or without HCl) to the HC process.

The HC process is typically operated at a pressure of 10 – 35 bars and a temperature of 500 – 600°C. Due to the high temperature combined with excess hydrogen and chloride chemistry, all known industrial HC reactor vessels, including internals and interconnecting piping are fabricated from Alloy 800H (Universal numbering system, UNS, N08810) or special modified Alloy 800H (also N08810) chemistry, also branded as Incoloy® 800H. The main composition of the Alloy 800H material is 30-35% Ni, 19-23% Cr and remaining Fe. The composition of minor elements Al, C and Ti differentiate Alloy 800H from Alloy 800 (N08800) and Alloy 800HT (N08811). Some industrial HC reactors are reported to be fabricated from Alloy 800HT (N08811), HR-120 (N08120) and 347 Stainless (S34700). However this is not confirmed.

One of the earliest HC fluidized bed reactor (FBR) vessel disclosures was by Union Carbide (Union Carbide 1979) of "Incoloy 800". There was not a definitive disclosure of the specific alloy but numerous personal communications through the years indicates the only Incoloy alloy considered and used by Union Carbide was Incoloy® 800H (N08810). As part of the continuing Union Carbide project, Mui and Seyferth (Mui and Seyferth, 1981), discussed specifically Incoloy 800H (N08810) as a preferred material of construction. This is further confirmed in an extended work by Mui (Mui, 1983), where more materials are studied and compared. A former custom industrial equipment fabricator located in the Netherlands, Verolme Special Equipment B.V. (ceased commercial operations in the early 2020's) (Verolme 2011) specified the use of modified Alloy 800H (still N08810) with tighter limits for minor impurities Al, C and Ti along with a special grain size.

The main purpose of building the laboratory test equipment was to study the effect of the silicon quality. Since the Incoloy material was known to be used in industrial reactors, we assumed that the best choice of reactor material would be Incoloy® 800HT (N08811) super alloy. At the time Elkem decided to build the HC lab (2004), more specific information about industrial HC reactor materials of construction was not commonly known. The differences between Alloy 800H (material used in known industrial reactors) and Alloy 800HT should not alter in any way the lab results. Experiments in small laboratory reactors are known to have more interaction with the reactor wall material than an industrial reactor due to the larger reactor wall surface to silicon weight ratio.

Surprisingly, we observed that the performance in the laboratory reactor was heavily influenced by the reactor material and the condition of the reactor wall. In this paper we will discuss the result of more than 20 years of struggle by running the laboratory reactor in Incoloy® 800HT and perhaps the companies running the HC process industrial scale could learn something from our experience.

2. RESULTS AND DISCUSSION

2.1 Reactor design

The main purpose of the apparatus is to measure the production of trichlorosilane (TCS). This is expressed as the so-called "TCS selectivity", which is the molar concentration of TCS in the product gas, excluding hydrogen. Other gas product species, as dichlorosilane, disilanes (Si-Si) and other high boilers (Si-O-Si) are also measured.

The reactant gasses are fed into the bottom of the reactor to react with the fluidized silicon powder. The product gasses and unreacted reactant gasses leave the reactor at the top and are

led through a filter system to a sampling system, to be quantitatively analysed by a gas chromatograph (GC). An automated needle valve downstream of the sampling system controls the pressure in the reactor system. As the silicon in the reactor is consumed, more silicon is automatically added to the reactor from the top to maintain a constant amount of 10g in the reactor. See figure 1 for more details.

All parameters and actions are fully automated, so the reactor can run without any need for attention between normal working hours. Normal runs last over 2-3 days, consuming 3-6 reactor volumes of silicon. Consuming one reactor volume means that 10g of silicon has been consumed and replaced by the addition system.

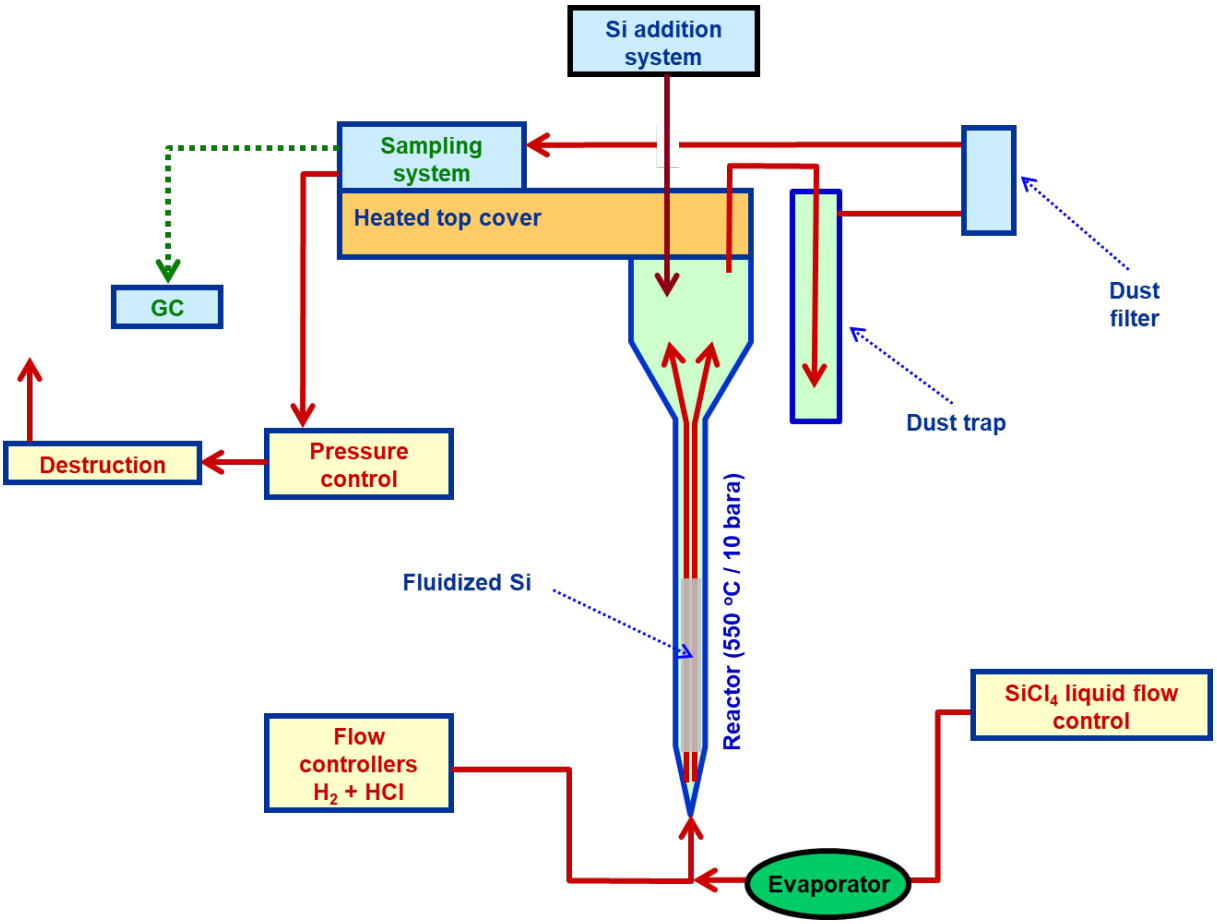


Figure 1: Flow scheme of the apparatus. Liquid silicon tetrachloride (STC) is evaporated and mixed with hydrogen and HCl gas before entering the reactor from the bottom. The silicon powder is fluidized by the upward flow of reactant gasses and product gasses. Overblown Si fines are removed from the product gas by a dust trap and a filter before the product gas enters the sampling system. The sampling system takes out a small volume of the product stream each 16-17 minutes, and send it to a gas chromatograph (GC) for quantitative analysis. The pressure in the reactor system is controlled by an automated needle valve downstream of the sampling system. Silicon powder is added to the reactor from the top to maintain 10 g of silicon in the reactor as silicon is consumed by the reaction.

2.2 Reactor performance deteriorating over time

To check the condition and reproducibility of the reactor, we make standard runs quite frequently. In a standard run, a specific standard Si material is tested with specific standard experimental conditions. These runs should all give equal results over time. However, we observed that the measured TCS selectivities of the standard runs started to become lower. An unfortunate consequence of this is that we cannot compare results between experiments spread over a longer period.

After a lot of investigation, we found that the reactor itself was the cause of the lower TCS selectivity. The selectivity went back up to a normal level after replacing it with a new reactor. See figure 2. All experiments were run with the same silicon sample and the same experimental conditions. The green runs were done when reactor A still was OK. The red runs were done in the same reactor after suspecting issues with the reproducibility. The blue runs were done in reactor B. This reactor was also one that had failed earlier, but it was re-machined internally to get fresh surfaces. As seen, the selectivity went almost up to the original selectivity, and with a good reproducibility

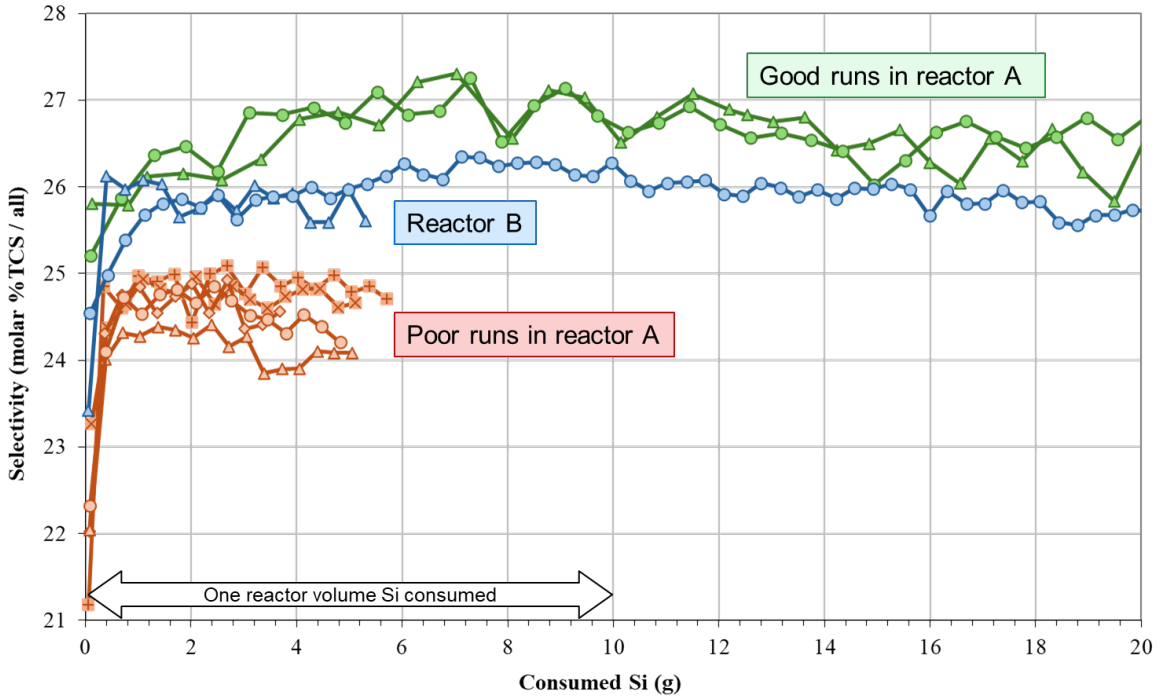


Figure 2: Comparison of TCS selectivities in different reactors and states of the reactors. The x-axis shows the progress as consumed silicon. The y-axis shows the TCS selectivity as the molar concentration of trichlorosilane (TCS).

2.3 The mechanism of reactor deterioration

Hoel and Rong found that oxygen, that was introduced to the reactor as oxide at the surfaces of newly added silicon particles, was able to migrate to older silicon particles and passivate their already active sites. This will in turn reduce the TCS production rate. However, these sites will eventually be reactivated. Selectivity will then also be given by how fast they can regenerate (Hoel and Rong, 2020).

Then it will be reasonable to suspect that oxides on the reactor walls can be sources for oxygen in the reactor as well. Larry Coleman explained that a silicide layer is formed on the reactor wall during the run. This silicide layer is protecting the reactor wall against further corrosion. However, when the reactor is stopped for maintenance and the reactor wall is exposed to humidity and air, this silicide layer will oxidize, and an oxide layer with a thickness of appx. 250 micron will peel off the inner reactor wall (Coleman, 2026). This is in good agreement with the conclusions of Mui and Seyferth (Mui and Seyferth, 1981) and an extended work by Mui (Mui, 1983). Based on that, we propose the following mechanism:

1. <u>During run (hot and with very limited access to oxygen):</u> Gas species with Si, e.g. TCS, will react with the reactor walls. This will allow Si atoms to migrate into the alloy and create a

silicide layer on the reactor surface. Kraus has studied how different alloy qualities corrodes in the HC process (Kraus 2002).

2. During maintenance (cold and with rich access to oxygen): This silicide layer will react with oxygen, creating a flaky layer of silicide oxides that peels of the surface. However, some oxygen will still remain on the inner reactor wall.
3. During next run: The silicide oxide layer will be a source for oxygen to passivate active sites, thus reducing the TCS selectivity. Industrial runs often last for a year. The remaining oxygen on the inner reactor wall will then have time to be consumed, and a protective layer of silicide will reappear on the remaining reactor alloy. This will make the reactor regaining its TCS selectivity. There are, however, not enough time for that in a typical lab run that last only a few days, so the TCS selectivity will not be regained.
4. Further runs and maintenances: In an industrial reactor, the silicide layer created in the previous run will peel off as oxide during each maintenance, and the wall will thus be thinner for each run. In a lab reactor, the silicide oxide layer will grow deeper and contain more oxygen. The TCS selectivity will be permanently reduced.

This mechanism is illustrated in fig 3.

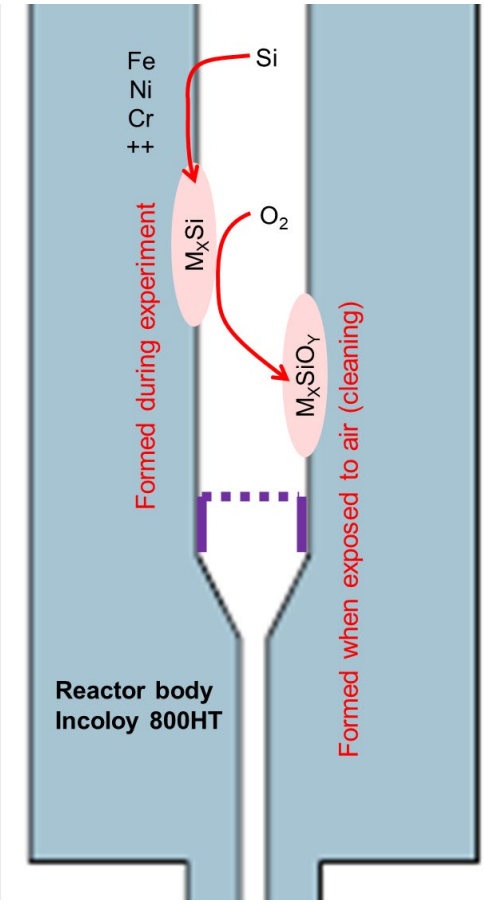


Figure 3: The assumed mechanism for creation of oxides. The left side shows the creation of silicides during experiments, while the right side shows creation of oxides during maintenance between the experiments.

2.4 Examination of the bad reactor

Reactor A was split along its vertical axis, to study the inner walls. One of those parts was cut into pieces small enough to fit into a scanning electron microscope (SEM) chamber. Se figure 4.

The SEM investigation revealed that there were mainly two types of surfaces, see overview in figure 5:

- Flaky material: See figure 6. The flakes contained significant amounts of Fe, Cr, Ni, Si and O. This surface has taken up high amounts of silicon and is partly oxidized.
- Material not covered by flakes: See figure 7. This area has probably been covered by flakes that eventually fell off. This material contained significant amounts of Fe, Cr, Ni and O, but much smaller amounts of Si. The different areas show different states of oxidation. The site "Spectrum 99" shows a surface with no oxidation yet. However, Si has started to infiltrate this site. At the other sites, oxidation has started. Those are probably future flakes.

Figure 8 shows a cross section cut of the inner reactor wall. Si is present not only in the grain boundaries, but also in the bulk reactor material. This shows that Si atoms migrate into the alloy, creating silicides with the metals in the alloy. We also can see that Si, O, and Cl has penetrated the reactor through channels or cracks.
This indicates that the flakes are a result of oxidation, and that the silicide oxidizes easier than the original alloy.

Figure 4: The pieces of the reactor that was examined by SEM. Pieces from left to right is from top to bottom

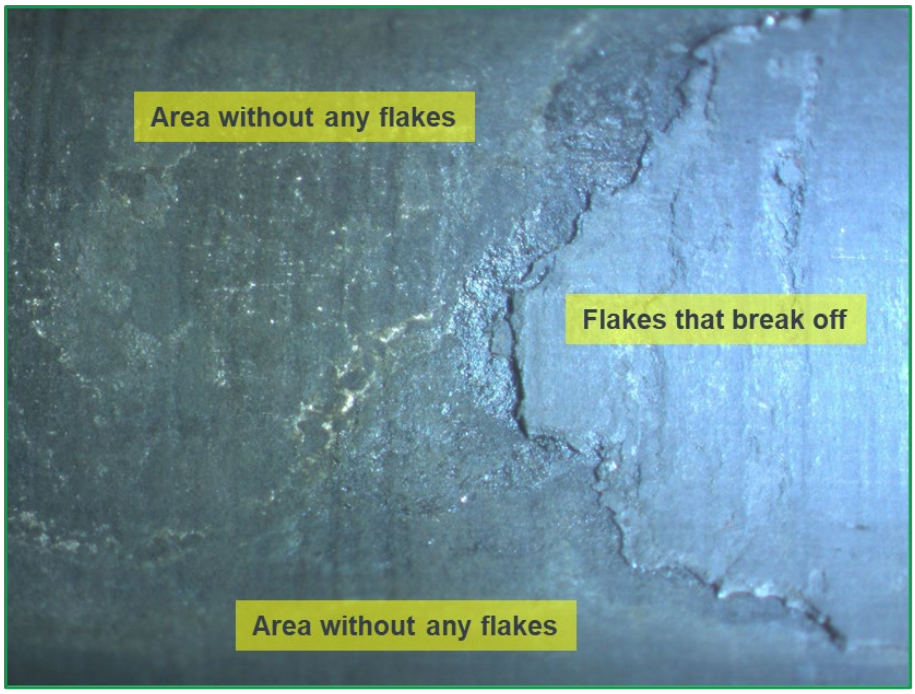
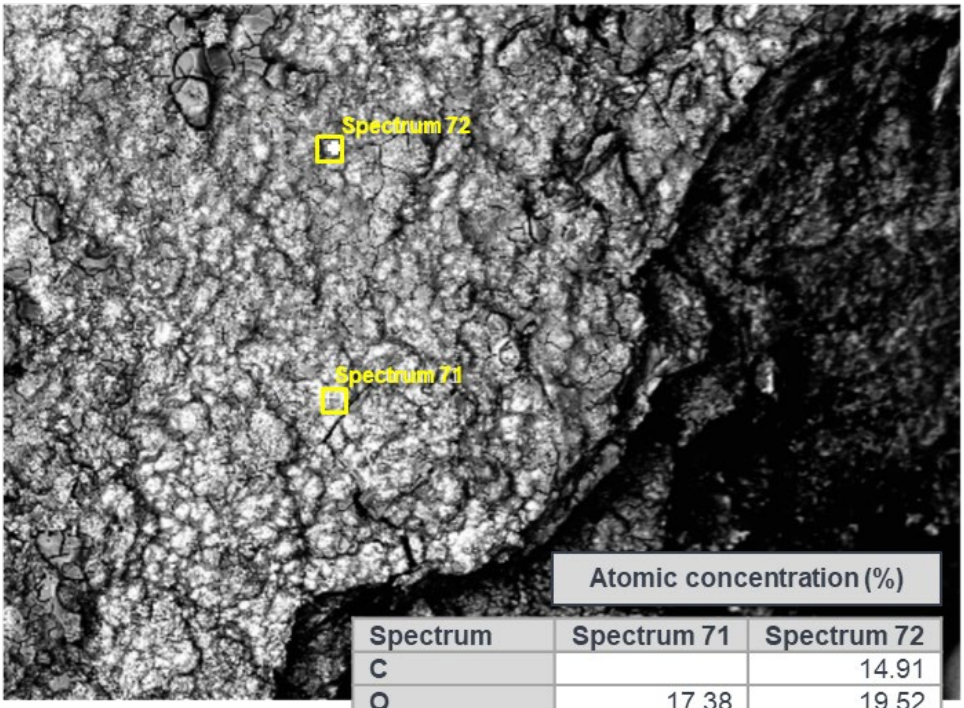


Figure 5: Light microscope picture of the inner reactor surface. Illumination is from the right. On the right side, there is a flake still attached to the reactor inner surface. The shadow line shows the left facing edge of the flake

To check the proposed mechanism for reactor deterioration further, an old reactor was washed thoroughly and then bored with the same diameter as the original bore (10mm) to remove deposits that could not be washed away with a brush. Surprisingly, a lot of torque was needed to re-bore through the reactor that was supposed to have an inner diameter equal to the bore used.

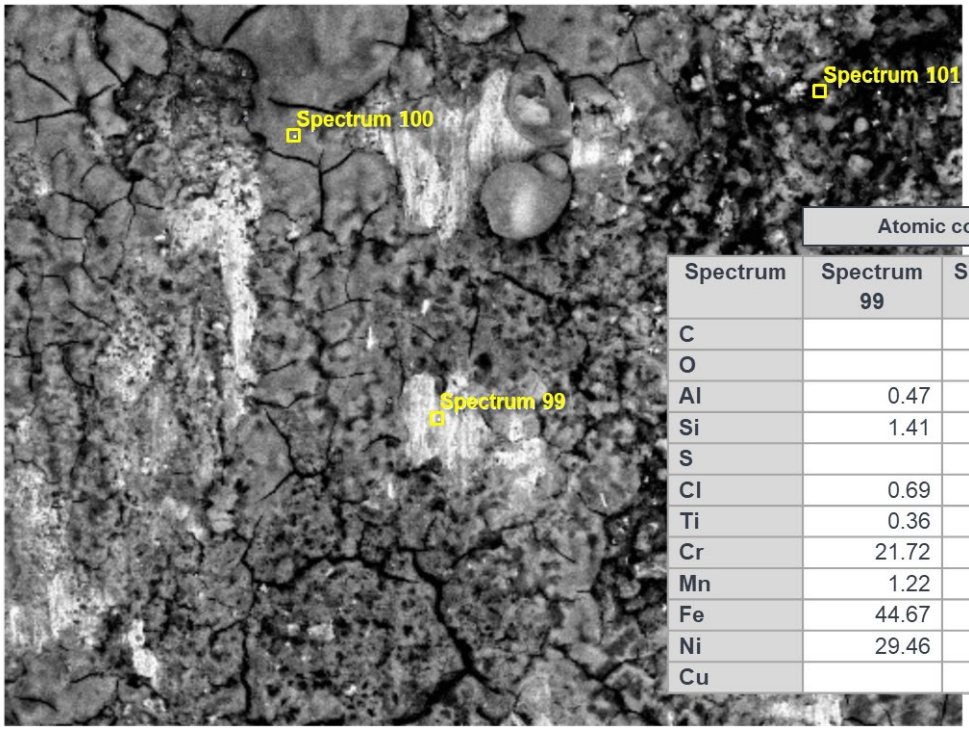
The drilling chips were examined by SEM and found to contain significant amounts of Fe, Cr, Ni, Si and O. An oxide layer should be easy to bore away, but a silicide layer probably not. As silicon atoms migrate into the alloy, they will occupy space, and the volume of the alloy will increase. This will in turn reduce the inner diameter of the reactor alloy, explaining the need for a high torque.

Figures 9 and 10 show SEM pictures of large pieces of the drilling chips, which are assumed to be pieces of the expanded reactor alloy that were cut off during the drilling. They have large amounts of Si in addition to the alloy components. The composition is quite inhomogeneous. Only one of the spectra detects oxygen. This spectrum is close to the surface of the drilling chip. This confirms that silicon species have reacted with the reactor walls to create a layer of silicides, which in turn has reacted with oxygen to create oxides at the reactor walls.



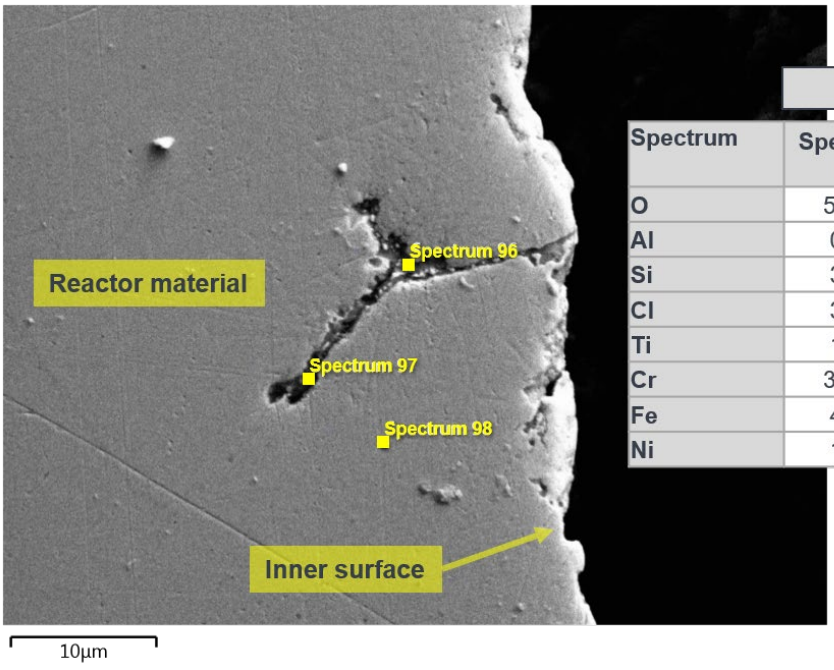
Atomic concentration (%)		
Spectrum	Spectrum 71	Spectrum 72
C		14.91
O	17.38	19.52
Si	24.19	18.76
Cl	2.77	6.26
Ti		3.61
V	0.41	
Cr	10.27	10.38
Mn		0.89
Fe	41.17	14.77
Ni	3.82	10.03
Mo		0.87

Figure 6: Flaky surface with high contents of Si and O in addition to the original reactor material



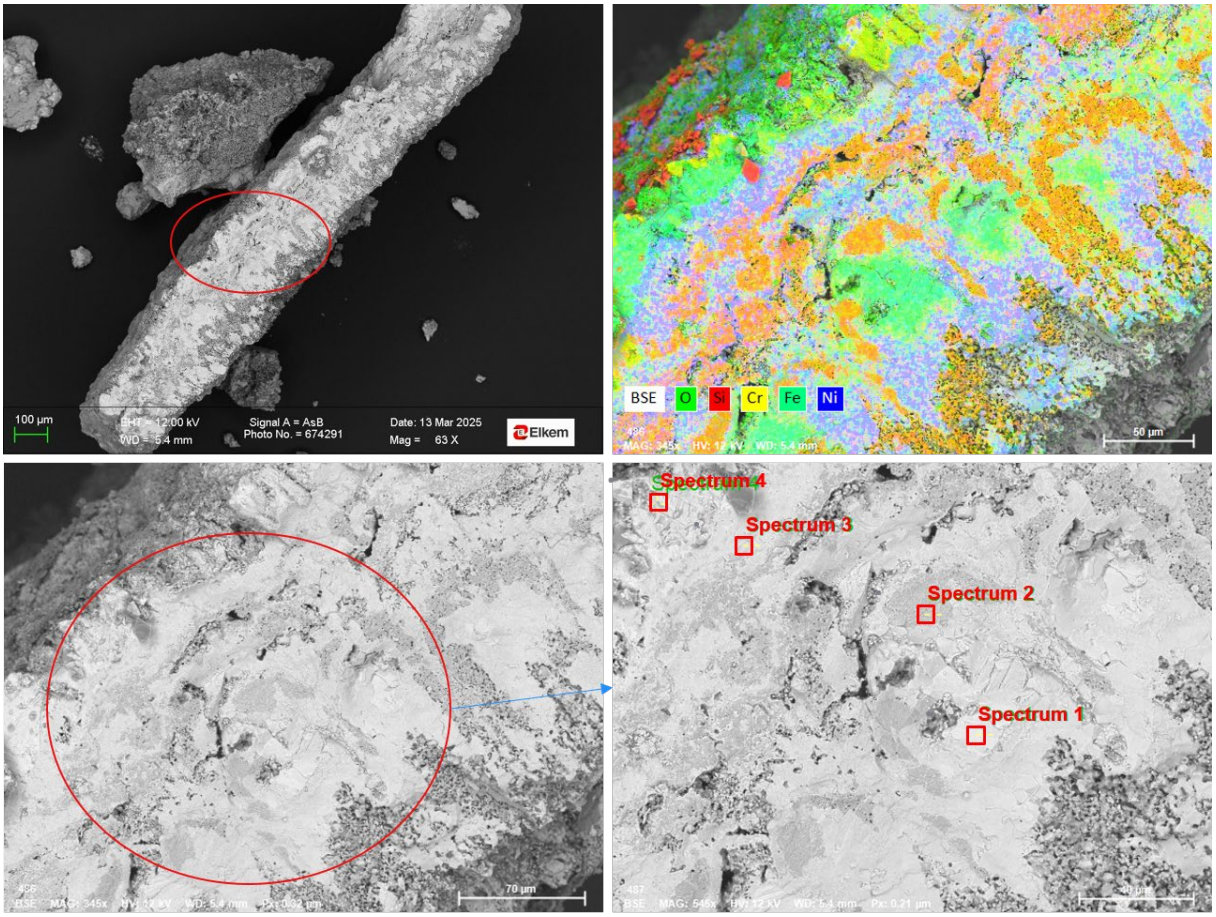
Atomic concentration (%)			
Spectrum	Spectrum 99	Spectrum 100	Spectrum 101
C			52.56
O		49.48	21.78
Al	0.47	0.07	0.18
Si	1.41	0.31	3.04
S			0.39
Cl	0.69	25.50	6.57
Ti	0.36		
Cr	21.72	2.11	6.06
Mn	1.22	0.27	0.20
Fe	44.67	6.35	4.57
Ni	29.46	15.91	4.34
Cu			0.32

Figure 7: Area not covered by flakes. The white areas are uncovered reactor alloy. In the point "Spectrum 99" very little corrosion has occurred yet. The dark areas are thin layers of oxidized reactor material with multiple cracks. In the points 100 and 101, the corrosion has started. Those sites are probably future flakes.



Atomic concentration (%)			
Spectrum	Spectrum 96	Spectrum 97	Spectrum 98
O	55,22	31,47	
Al	0,45		0,83
Si	3,06	2,64	2,43
Cl	3,54	1,69	
Ti	1,11	0,85	
Cr	31,20	27,12	26,19
Fe	4,28	25,10	45,51
Ni	1,15	11,13	25,03

Figure 8: Cross section of the inner reactor surface. Spectrum 98 shows that Si has migrated more than 10 microns into the reactor bulk material. The two other spectra shows that Si, O, and Cl has penetrated the reactor through channels or cracks.

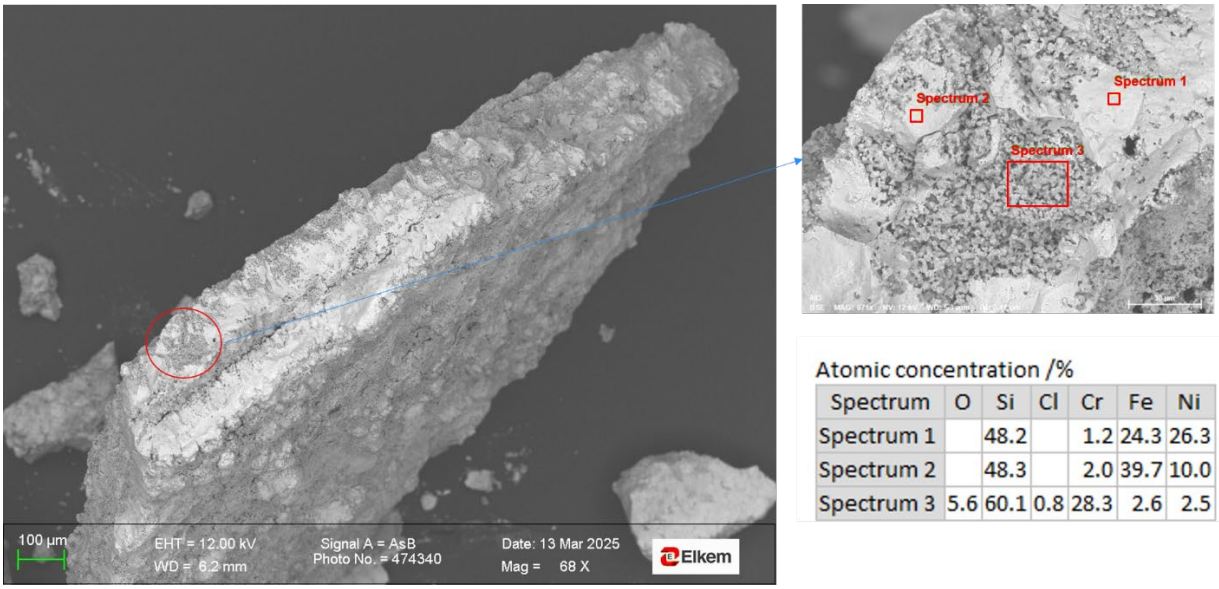


Atomic concentration /%

Spectrum	Si	Cl	Cr	Fe	Ni
Spectrum 1	26.3		2.3	70.0	1.3
Spectrum 2	57.3		27.2	9.2	6.4
Spectrum 3	52.6		2.6	18.7	26.1
Spectrum 4	25.3	0.5	7.2	62.0	5.0

Figure 9: SEM picture of one of the large drilling chip pieces from boring through the reactor. This piece is a mix of silicides with Fe, Ni and Cr. There is no oxygen. This indicates that this is a part of the alloy itself, that expanded due to the infiltration of Si atoms. This corresponds with the high torque needed to bore it out

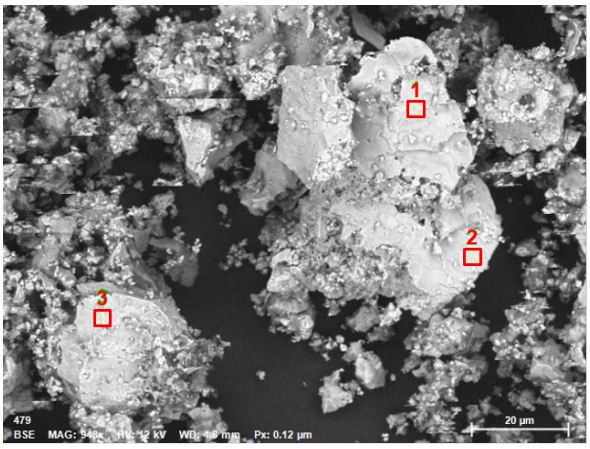
Figure 11 shows SEM pictures of the smaller drilling chips. These particles contain significant amounts of oxygen as well as Fe, Ni, Cr and Si. This indicates that these are silicide oxides that were easy to crush and machine away from the reactor wall. These small pieces are probably remainders of flakes that still were too rigid to wash away with a brush.



Atomic concentration /%

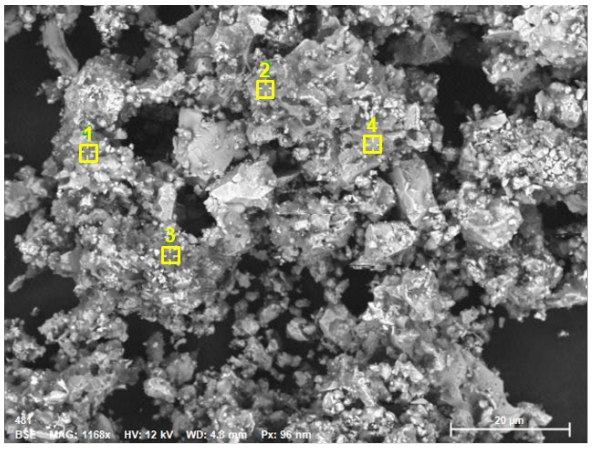
Spectrum	O	Si	Cl	Cr	Fe	Ni
Spectrum 1		48.2		1.2	24.3	26.3
Spectrum 2		48.3		2.0	39.7	10.0
Spectrum 3	5.6	60.1	0.8	28.3	2.6	2.5

Figure 10: SEM picture of another large drilling chip piece from boring through the reactor. This piece is also a mix of silicides with Fe, Ni and Cr. There is some oxygen on the area spectrum that is close to the surface.



Atomic concentration /%

Spectrum	O	Si	Cr	Fe	Ni
1	6.3	50.8	1.7	18.6	22.5
2		49.2	2.3	25.4	23.0
3	5.9	47.1	1.1	40.4	5.5



Atomic concentration /%

Spectrum	O	Al	Si	Cl	Ca	Cr	Mn	Fe	Ni
1	4.1		42.8	1.7		8.9		24.8	17.6
2	37.4		38.6	1.8		3.4	0.6	11.0	7.2
3	30.7	3.9	54.6	2.1	2.0	0.8	0.5	4.5	0.9
4	36.3		28.7	7.1		8.5		11.6	7.8

Figure 11: SEM pictures of the smaller particles in the drilling chips from boring through the reactor. These particles contain significant amounts of oxygen as well as Fe, Ni, Cr and Si. This indicates that these are silicide oxides

2.5 Differences between laboratory and industrial operation of the HC process

The industrial HC process is a continuous process where the process can be operated about one year before the reactor system is stopped for maintenance. Contrary to this, a lab scale reactor normally is operated for only a few days between each maintenance. The main reason for this, is to make a full reset of the system between each experiment. This ensures that an experiment is not influenced by the previous experiment.

One consequence of the frequent maintenances is that the inner reactor walls will be exposed to air much more frequently than in an industrial reactor, making this oxidation issue much greater in a lab than at an industrial plant.

2.6 Addressing the laboratory reactor issues

To reduce the oxidation to a minimum, the reactor is immediately connected to an argon supply after emptying it, and flushed continuously while the other parts of the reactor are prepared for the next run. When all these other parts are readied and mounted, the reactor is washed quickly as possible with isopropanol, mounted, evacuated and put on argon flush. In addition, the apparatus is always on continuous Ar flush when "not in duty". We observed a positive effect of minimizing exposure to oxygen during maintenance. However, we cannot do the cleaning without any exposure to air.

Therefore, we have to live with the fact that reactors will deteriorate, also in the future. To reduce the practical and economic consequences of this, a new reactor design with replaceable inner reactor liner has been developed. This makes it easier and cheaper to replace the inner walls of the reactor when needed. This replacement will probably follow "hard time" maintenance principles, by being replaced after a specific number of runs regardless of condition. This will ensure a stable performance of the reactor. We have not concluded yet how many runs each reactor liner can be used before replacement.

This new design also allows easy and cheap changes of reactor material, if desired for the sake of research.

3. CONCLUSIONS

It has been found that the performance of the hydrochlorination process (HC) deteriorates over time, due to corrosions of the reactor inner walls. This has been studied in an Incoloy® 800HT (N08811) reactor at a reactor temperature of 550 ^{o}C and an absolute pressure of 10 bar. We believe that our conclusions also apply to a reactor constructed of Incoloy® 800H (Alloy 800H; N08810), which matches the known material used in many industrial reactors.

Under these conditions, silicon containing gas species will react with the reactor wall, to create silicides of Fe, Ni and Cr. The Si atoms migrate several micrometres into the reactor bulk material.

The formation of silicides on the reactor internal wall destroys the protective properties against corrosion, even of super alloys like Alloy 800HT (N08811). The outer layer of silicides at the reactor walls oxidizes when in contact with air, and will eventually flake off as silicide oxides. This process will continue at the new surfaces behind the flaking.

The peeling of the silicide layer (250 micron thickness) will make the reactor wall thinner after each run. Therefore, an industrial reactor can be exposed to air only a limited number of times before it must be replaced as the design corrosion allowance will have been exceeded. In addition, we observe channels of silicides and chlorides. They can go further into the reactor wall, increasing the potential risk for more dangerous, and difficult to predict, leakages.

Oxygen from the oxidized silicides will in turn contribute to passivate active sites at the silicon powder surfaces in the reactor. The HC process is a reaction from STC to an equilibrium mixture of STC and TCS, see equation 1. The over-all reaction rate in the reactor will become

lower when the surface area of active sites is reduced. This will in turn reduce the amount of TCS produced during the available residence time in the reactor.

Finally, we should note that this work is limited to the HC process chemistry that does not include any external co-feed of anhydrous HCl; only the "classic" HC system of Si, H_2 and STC has been investigated. However, we have recently implemented the option to feed anhydrous HCl into the reactor.

4. ACKNOWLEDGEMENTS

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