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LACK OF WEATHER & AIR QUALITY DATA

The air quality data and analysis provided by PacWest are insufficient for both for the environmental impact statement and permitting. In terms of predicting real impacts on the communities and environment in the vicinity of the smelter, it is a very bad joke! The company is attempting to obtain regulatory decisions based ONLY on a model, with no pertinent local /regional air quality or weather data to test the model and to provide reasonable predictions of air quality impacts. I urge the DOE to halt this streamlined DEIS process and start over; certainly it should not issue any permits. Why do I ask this?

PacWest claimed last year that it would collect one-year's worth of data, but where are those data? From what locations?

PacWest claims it is not able to provide SO₂ emissions control at the Newport location. By not controlling SO₂ emissions, both people and the environment will be at greater risk due to PacWest's operations in eastern Washington and north Idaho, and possibly beyond. What is the increased health risk for both humans and the environment if PacWest does not provide SO₂ emission control? (If the PacWest refuses to provide such emission controls, what's the point of a permit.) Perhaps PacWest should stay in Canada and find a location where physical constraints do not limit its ability to pollute.

Another major issue I have with PacWest and the DOE is the bait and switch game on air quality data submitted for this EIS. During the process, it has come to my attention that the calculations on major pollutants, and possibly modeling results, have been changed. I noted lower numbers on some pollutants but the total amount of greenhouse gases had increased. How and why these projected data changed must be explained.

Furthermore, it is inappropriate for the DOE to allow such changes mid-stream in this process. This is unfair to the residents of the communities that will be impacted, as well as placing a burden on our legal and environmental advocates to come up with last-minute new analyses. Changing the data related to significant impacts can be considered illegal, too. Frankly, I think the DOE should stop this charade, and not attempt an EIS for this smelter until there are firm and sufficient data, i.e. not changing according to PacWest's latest submissions.

As further evidence of the lack of any scientific air data for this EIS, there is no National Weather Service-certified weather station in the vicinity of Newport. The closest certified station is at Deer Park, WA, which is not only too far away, but in a different topographic region. Where is PacWest going to obtain valid weather data?

Similarly, there are insufficient air quality monitoring stations. I will address the Idaho side of this issue. The Idaho Department of Environmental Quality (IDEQ) has automatic monitoring stations in Bonners Ferry and Sandpoint that ONLY measure particulates—PM 2.5 and PM 10—and some basic weather measurements which aren't certified. The closest community to the smelter is Oldtown, for which there appear to be NO data. I have found no other data for this region of Idaho. See attached Map. The weather in the area varies considerably from year or year, and the wildfire smoke also skews the data seasonally, so one year of data collection is inadequate. How are the DOE and the IDEQ going to address the lack of both weather and air quality data for permits?

There should also be monitoring for more than particulates. It should include the expected major gases from the smelter. Baseline data also has to be collected for such things as VOCs and heavy metals, which the smelter is expected to emit. Attached is an air monitoring report from the vicinity of a smelter in Iceland, see VOC measurements in vicinity of a silicon smelter. How are PacWest and the DOE going to collect these type of data BEFORE and AFTER permits are issued?

Beyond the basic pollutants associated with coal and wood burning, the silica smelting technology proposed by PacWest creates a number of other pollutants that impact occupational, public and environmental health. These have been studied to some degree, mostly in Norway and China. Will the DOE do a literature review to figure out what other pollutants, and their quantities and areal extent, are likely to be emitted from this problematic smelter? For starters, I have uploaded some recent technical articles that I expect the DOE to review and to provide answers as to their applicability to PacWest's smelter pollution.

I submit that PacWest should be required to pay for a network of air quality monitoring and weather stations in a minimum 100-mile radius of the smelter in both Idaho and Washington, for at least three (3) years. This should be done before attempting a new or revised EIS, and certainly before any permit applications. What will the DOE and IDEQ do to ensure collection of adequate air quality and weather data in both states? What will the agencies do to obtain baseline data for other pollutants such as heavy metals, radionuclides, etc.?

VOC measurements in vicinity of a silicon smelter Passive air sampling around United Silicon, Iceland Norbert Schmidbauer, Espen Mariussen NILU report 35/2017 © NILU Norwegian Institute for Air Research The publication may be freely cited where the source is acknowledged NILU's ISO Certifications: NS-EN ISO 9001 and NS-EN ISO 14001. NILU's Accreditation: NS-EN ISO/IEC 17025. 2 NILU report 35/2017 NILU report 35/2017 CLASSIFICATION: C C Confidential DATE 04.10.2017 SIGNATURE OF RESPONSIBLE PERSON Ole-Anders Braathen, Dep.dir. (sign.) NUMBER OF PAGES 25 TITLE VOC measurement in vicinity of a silicon smelter Passive air sampling around United Silicon, Iceland PROJECT LEADER Hilde Thelle Uggerud NILU PROJECT NO. O-117066 AUTHOR(S) Norbert Schmidbauer, Espen Mariussen QUALITY CONTROLLER Hilde Thelle Uggerud REPORT PREPARED FOR Multiconsult ASA, Nedre Skøyen vei 2, 0276 Oslo Tom Arild Olsen CONTRACT REF. [Skriv ref] ABSTRACT On behalf of Multiconsult ASA, a pilot study of VOC within and around a silicon smelter, United Silicon, has been carried out. The silicon smelter is located at Reykjanesbær in Iceland. 10 Tenax tubes were used as passive samplers and placed in a residential area and close to the silicon smelter, both inside and outside the plant. The samples were taken between 21.05.2017 and 23.06.2017. The concentrations found are typical for outdoor air in summertime. High values of anhydrides were found in samples collected inside the baghouse. Otherwise, the concentrations were low. To identify a possible daily profile of the gas composition in the emissions during startup and shutdown of the silicon smelter, 12 samples were taken from inside the baghouse, by the use of evacuated gas-sampling cylinders. 1-3-5- Trioxane which is a polymerisation product of formaldehyde, are present in these samples. This indicate higher concentrations of formaldehyde, which is not covered by the measurement technique used. NORWEGIAN TITLE VOC-mållinger rundt et silisiumsmelteverk, Passiv prøvetaking rundt United Silicon, Island KEYWORDS [Skriv stikkord] [Skriv stikkord] [Skriv stikkord] ABSTRACT (in Norwegian) På oppdrag fra Multiconsult ASA, har det blitt utført en pilotstudie av VOC rundt silisiumsmelteverket United Silicon. Smelteverket er lokalisert i Reykjanesbær i Island. 10 Tenaxrør ble brukt som passive prøvetakere og plassert i et boligområde nær smelteverket, samt inne i fabrikken og på utsiden av denne. Prøvetakingen foregikk i perioden 21.05.2017 til 23.06.2017. Konsentrasjonene funnet i boligområdet er typiske for uteluft ved sommertider. Høyere verdier av anhydrider ble funnet i prøvene fra innsiden av posehuset. Ellers var konsentrasjonene lave. For å identifisere en mulig daglig profil av gassammensetningen i utslippet ved oppstart og nedstenging av verket, ble det tatt 12 luftprøver inne i posehuset, ved bruk av evakuerte gassflasker. I disse prøvene ble det funnet 1-3-5- Trioxane, som er et polymerisasjonsprodukt av formaldehyd. Funnet kan tyde på at formaldehyd er tilstede, men mållemetoden som er benyttet her er ikke egnet for bestemmelse av denne forbindelsen. PUBLICATION TYPE: Digital document (pdf) COVER PICTURE: Source:

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Summary On assignment from Multiconsult ASA, a pilot study of VOC within and around a silicon smelter, United Silicon, has been carried out. The silicon smelter is located at Reykjanesbætur in Iceland. 10 Tenax tubes were used as passive samplers and placed in a residential area and at the silicon smelter, both inside and outside the plant. The samples were taken between 21.05.2017 and 23.06.2017. The VOC concentrations found in the residential area are typical for outdoor air in summertime. The concentration found in the furnace house is rather low, emissions in the very low milligram per m³ range can be considered as quite clean industrial processes where combustion of wood or coal is involved. The composition of the samples do not show uncommon compounds for combustion processes where wood is involved. The samples taken inside the baghouse are showing high concentrations of Phenyl maleic anhydride and in addition, other anhydrides at lower concentrations. Anhydrides are irritants to skin, eyes and the respiratory system. The same compounds are also found in the samples taken outside the baghouse, but at far lower concentrations. To study the daily profile of the gas composition in the emissions during startup and shutdown of the silicon smelter, 12 samples were taken from inside the baghouse, by the use of evacuated gas-sampling cylinders. Overall, the concentration levels of the compounds found are quite low. However, 1-3-5- Trioxane which is a polymerisation product of formaldehyde, is present in the samples. This indicate higher concentrations of formaldehyde, which is not covered by the measurement technique used. 4 NILU report 35/2017 VOC measurements in vicinity of a silicon smelter Passive air sampling around United Silicon, Iceland 1 Introduction The purpose of the VOC (volatile organic compounds) measurement campaign was to identify compounds in the emissions from United Silicon's Factory that may have a potential as irritants for the surrounding habitants. The VOC campaign consisted of 3 different parts. One should cover VOC-concentrations at a background site and within the habituated vicinity of the factory, the second should focus on daily VOC-profiles within the factory during startup and shutdown, while the third should focus on VOC-emissions within the furnace house and the baghouse and in addition cover diffusive emissions from the factory as a whole. 1.1 Sampling method Our approach was based on non-target screening - the choice of sampling and measurement techniques is based on semi-quantitative broadband methods. NILU has more than three decades of extensive experience with VOC measurements in indoor, outdoor, industrial, rural, urban and background environment. Several thousand measurements during that time period have been used to build up a database of several hundred compounds which are common in those environments. The database is used, together with several other commercially available mass spectra databases, to identify VOCs taken on adsorption tubes. Sampling with adsorption tubes can be done by means of a pump (active sampling) or by diffusive sampling (passive sampling). For VOC broadband measurements - Tenax TA is the preferred adsorbent. The content on the sample tubes is thermo desorbed at the laboratory, focused on cold traps (-30°C), separated on a Gas Chromatograph and detected by a Mass Spectrometer. Because of the very short time between the involvement of NILU into the project and the startup of the measurements, those robust and broad VOC measurement techniques have been chosen. VOC is a complex group of compounds spreading from hydrocarbons, halocarbons, aromatic compounds, ketones and aldehydes, organic acids, ethers, N and S containing compounds. On Tenax adsorption tubes most of those compounds can be sampled and analyzed - but since the volatility of the compounds is covering a range from a boiling point of 10 to 300 °C not all compounds are sampled in the same quantitative matter. On the other hand - the tubes give on a relative base - very comparable results. Some compounds that could occur in the emissions of a silicon factory, like Formaldehyde and Acetaldehyde or COS, will not be detected by the chosen measurement technique, because of their high volatility. Compounds bound to particle emissions will also not be detected. The most high-boiling compounds to be detected are 3-ring PAHs. 5 NILU report 35/2017 2 Part 1: VOC in living areas surrounding of the factory One passive sample was taken in a residential area between the 17 and 27 June 2017 - the sample was marked - Garden South. The results are shown in Table 1. Table 1: VOC result from sample taken in residential area

Sampling site	Sample id/tube id	Sampling period	Component
Garden South			Nonanal
			1-Butanol
			Acetic acid

2,2,4,6,6-pentamethyl heptane Hexanal Cyclopentane Toluene 1-Octene Octanal hexamethyl cyclotrisiloxane (D3) Decane Hexane 3-carene Heptanal 2-ethyl-1-hexanol Cyclopentane, methyl-octamethyl cyclotetrasiloxane (D4) 2-methylpentane 2-Hexene decamethyl cyclopentasiloxane (D5) Butanal alfa pinene Nonane Limonene 2-hydroxy benzaldehyde (salicylaldehyde) p-and m- Xylene (1,4 og 1,3 dimethylbenzene) Pentane Undecane Dodecane 1-ethoxy-2-propanol Total concentration of identified compounds Number identified components Total concentration of volatile compounds (TVOC) Number of components included in TVOC (conc. > 0,1 \hat{I} ¼g m-3) Sample received Sample analysed NILU report 35/2017 Garden south Id 214 17-27 June 2017 Concentration Toluene-equivalents (\hat{I} ¼g m-3) 16,8 7,3 5,3 5,2 4,8 4,6 4,4 3,6 3,4 3,2 3,0 2,6 2,5 2,2 2,2 2,0 2,0 1,8 1,8 1,8 1,6 1,2 1,1 1,1 1,1 1,0 0,8 0,8 0,8 0,7 CAS no 124-19-6 000071-36-3 000064-19-7 13475-82-6 000066-25-1 287-92-3 108-88-3 000111-66-0 124-13-0 541-05-9 124-18-5 110-54-3 13466-78-9 111-71-7 104-76-7 000096-37-7 556-67-2 107-83-5 000592-43-8 541-02-6 000123-72-8 80-56-8 000111-84-2 138-86-3 90-02-8 106-42-3 109-66-0 1120-21-4 112-40-3 1569-02-4 35 202 102,1 149,8 29 June 2017 06 August 2017 6 2.1 Results and discussion The total amount of VOC is 150 \hat{I} ¼g/m³. This is a typical concentration for outdoor air in a residential area in summertime. As a comparison, Indoor air concentrations of VOC in European houses are normally between 100 and 250 \hat{I} ¼g/m³. The main sources are emissions from vehicles and building materials and atmospheric degradation products. Vehicles emissions are toluene, xylenes and alkane hydrocarbons ranging from pentane to pentadecane. Building material emissions are mono-terpenes like alfa- pinene , 3- carene and limonene from wood and vegetation; siloxanes are quite common emissions from all kind of artificial material and are to be found both indoors and outdoors; aldehydes like hexanal, heptanal, octanal and nonanal are oxidation products mostly from a reaction of tropospheric ozone with all kind of hydrocarbons and the photochemically induced degradation of hydrocarbons by sunlight. There are no compounds in the sample which are showing unusually high concentrations and there are no compounds among the 35 with the highest concentrations which are not normal to be found in background air or suburban or urban air. And most important \hat{a} the compounds with the highest concentrations measured in the furnace house and inside the baghouse \hat{a} naphthalenes and anhydrides are not detected in the sample. 3 Part 2: Flask sampling during startup and shutdown of the factory The samples of the daily profiles during startup and shutdown of the factory were taken with evacuated gas-sampling cylinders and transferred to Tenax tubes at NILU. The samples were taken inside - on top of the bag house - as spot samples within 15 minutes once every day between May 21 and June 1. Sampling using canisters is mostly suited for the light fraction of VOC \hat{a} starting with light boiling compounds like acetone and ending with naphthalene. In all of the 12 samples were about 50 compounds which are in a concentration range that enables a positive identification. The results of the most dominating compounds and compounds normally not present in outdoor air are summarized in table 2 In a search for uncommon compounds and known irritants the most common compounds normally to be found in outdoor air like Benzene, Toluene or Xylenes or C7 to C20 Alkanes are excluded in further discussions. Overall - the concentration levels of the compounds are quite low \hat{a} ranging from a few \hat{I} ¼g/ m³ to 3 mg/m³. The compounds with the highest concentrations are siloxanes and are most probably not from the furnace processes, but from building materials within the factory \hat{a} most probably the bag house and its inventory. As an overall evaluation of the 12 samples we would conclude, that we (with the used method) could not identify any compound at concentration levels, which could have effects on the population in surrounding villages. A conservative assumption of the dilution of 10 to 100 thousand would still give very low doses at those sites. 7 NILU report 35/2017 There is however a compound which could be taken into closer considerations for further investigations. 1-3-5-Trioxane (Cas nr 110-88-3) is a polymerization product of formaldehyde. The concentration levels are not very high \hat{a} between 13 and 53 \hat{I} ¼g/m³, but its presence should indicate far higher concentrations of formaldehyde. Formaldehyde is not covered by our measurement method - but there are several quite simple measurement techniques available for both active and passive sampling of formaldehyde. The formation of Formaldehyde within the processes of the factory are

very likely and could probably vary to a high extent during the processes of startup and shutdown. Formaldehyde is a known irritant and very much is known about its health effects. Table 2 Results from analysis of air sampled in evacuated canisters ($\hat{1}\frac{1}{4}$ g m⁻³) NILU report 35/2017 Component Cas no Sampling date May 21 May 22 May 23 May 24 May 25 May 26 May 27 May 28 May 29 May 30 May 31 June 1 Trioxane 110-88-3 13 12 13 17 16 24 19 56 14 27 23 13 Siloxane-D3 541-05-9 80 212 245 171 930 385 640 1204 248 367 1526 346 Dimethylaminoacetonitrile 926-64-7 0 3 28 10 39 40 61 65 24 26 46 31 Nitroso dimethylamine 62-75-9 0 0 15 0 31 21 26 68 16 24 38 14 Siloxane-D4 556-67-2 59 138 90 128 913 515 498 2387 234 392 3045 247 2-ethyl-1-hexanol 411-44-8 36 43 33 84 25 23 51 109 19 56 52 27 Naphthalene dione 2906-90-3 139 174 188 220 167 161 190 441 122 154 197 194 Naphthalene 91-20-3 5 6 16 17 22 6 22 64 15 9 18 21 4 Part 3: Emissions at the factory

In this sampling approach the focus was on VOCs emissions within the furnace house and the baghouse and in addition cover diffusive emissions from the factory as a whole. Having in mind that the emissions from the top of the bag house are the bulk part of the factory emissions, while the gases measured in the furnace house only contribute to a less extent to the total emissions. The sample taken outside the roof of the baghouse should give a good indication of the factories diffusive emissions.

4.1 Emissions within the furnace house Inside the furnace house three samples were taken over the periods 21th May to 9th June , 9th June to 16th June and 16th June to 23rd June. The samples were taken on Tenax tubes based on diffusive sampling. The sampling sites are shown in the pictures following the report.

4.2 Results and discussion The results are an average concentration over the whole sampling period of 19 days for the first period and one week for the others. A compound could be emitted in very high concentrations at a shorter time period and low concentrations at others, but still show an average concentration like another compounds which is not varying at all during the whole period. Another important fact is that the calculated concentration using diffusive sampling is very temperature dependent. The known uptake rates for Tenax tubes are normally valid for 8 ambient temperatures. A temperature of 20 degrees higher could lower the uptake rate by 50 % so that the reported concentrations are underreported by a factor of 2. The results are shown in the detailed sample reports at the end of this section. The total concentration of about 200 detectable compounds is about 750, 850 and 1100 $\hat{1}\frac{1}{4}$ g/m³. In all three samples, the 40 compounds with the highest concentrations account for about 66% of the total VOC concentration. There are two groups of components - which account for over 80 % of the concentration of the identified compounds. The first group are Naphthalene and its derivatives together with light PAHs and the other group consists of alkane hydrocarbons and light aromatic compounds. The total concentration is rather low, emissions in the very low milligram per m³ range can be considered as quite clean industrial processes where combustion of wood or coal is involved. The composition of the samples do not show uncommon compounds for combustion processes where wood is involved. The bulk part of the exhaust from the furnace house, as it is measured here, will not be emitted to the outdoors and it undergoes an extensive oxidation process before it enters the baghouse. Only diffusive emissions from the furnace house will show the pattern of the samples taken inside the furnace house. Naphthalenes, light PAHs and aromatic compounds show low odour threshold to humans. The composition and concentration levels of the three samples would definitely be detectable by humans and the odour could definitely be associated with burnt materials. And even a dilution of some tens to hundreds could still be detected by a human nose. We cannot exclude that there could be certain meteorological conditions where diffusive emissions from the factory could be noticed in the surroundings of the factory but in average the dilution would be several factors higher and it will not be possible to smell those emissions. The sample taken at Garden South shows no evidence for long term conditions of naphthalene emissions.

9 NILU report 35/2017 Table 3 VOC from sample taken inside the furnace house NILU report 35/2017 Sampling site Sample id/tube id Sampling period Component Naphthalene Naphthalene, 1-methyl- styrene (ethenylbenzene) Dibenzofuran Acenaphthene Naphthalene, 2-methyl- Biphenylene tetradecane hexadecane phenol toluene Naphthalene, 1,6-dimethyl- tridecane pentadecane o-xylene (1,2-dimethylbenzene) Naphthalene, 2,3-dimethyl- dodecane Biphenyl

Anthracene octadecane benzene benzaldehyde Naphthalene, 1,4-dimethyl- undecane Naphthalene, 2-ethyl- nonadecane acetophenone octamethyl cyclotetrasiloxane (D4) 1,1'-Biphenyl, 4-methyl- 1H-Inden-1-one, 2,3-dihydro- 1-methoxy-2-propyl acetate 2,6,10-Trimethyltridecane Naphthalene, 1,2,3,4-tetrahydro-1,4-dimethyl- 1,2-Naphthalenedione Benzene, 1-ethenyl-2-methyl- Benzene, 2-ethenyl-1,4-dimethyl- p-and m- Xylene (1,4 og 1,3 dimethylbenzene) Total concentration of identified compounds Number identified components Total concentration of volatile compounds (TVOC) Number of components included in TVOC (conc. > 0,1 $\hat{I}^{1/4}$ g m-3) Sample received Sample analysed USI-2 Furnace house Id 701 21 mai-9 June 2017 Concentration Toluene-equivalents ($\hat{I}^{1/4}$ g m-3) 51,3 36,6 34,5 26,0 25,0 22,9 15,7 15,0 13,6 13,3 12,9 12,0 11,5 11,4 11,3 10,7 10,6 10,6 10,1 8,5 8,4 8,4 7,7 7,3 7,0 6,2 6,1 6,0 6,0 5,6 5,5 5,2 5,2 5,2 5,1 4,9 4,7 CAS no 000091-20-3 000090-12-0 100-42-5 000132-64-9 000083-32-9 000091-57-6 000259-79-0 629-59-4 544-76-3 108-95-2 108-88-3 000575-43-9 629-50-5 629-62-9 95-47-6 000581-40-8 112-40-3 000092-52-4 000120-12-7 593-45-3 71-43-2 100-52-7 571-58-4 1120-21-4 000939-27-5 629-92-5 98-86-2 556-67-2 000644-08-6 000083-33-0 108-65-6 003891-99-4 004175-54-6 000524-42-5 000611-15-4 002039-89-6 106-42-3 37 212 468,1 763,4 16 June 2017 19 June 2017 10 Table 4 VOC from sample taken inside the furnace house NILU report 35/2017 Sampling site Sample id/tube id Sampling period Component naphthalene o-xylene (1,2-dimethylbenzene) Acenaphthene 2-methylnaphthalene Heptadecane 1-methylnaphthalene tetradecane tridecane hexadecane pentadecane dodecane Toluene nonanal phenol Biphenylene Naphthalene, 2,7-dimethyl- Naphthalene, 2,3-dimethyl- Octadecane 2-phenoxyethanol benzaldehyde undecane 1,1'-biphenyl p-and m- Xylene (1,4 og 1,3 dimethylbenzene) nonadecane decane Naphthalene, 1,6-dimethyl- octamethyl cyclotetrasiloxane (D4) Naphthalene, 1,3-dimethyl- 3-methyltetradecane acetophenone Benzene, 1-methyl-4-(2-propenyl)- 1H-Indene, 2,3-dihydro-1,1,3-trimethyl-3-phenyl- Naphthalene, 1,2,3,4-tetrahydro-6-methyl- benzene Nonadecane, 9-methyl- 2-methyltridecane 2,2,4,6,6-pentamethyl heptane Phenanthrene 1-Butanol Total concentration of identified compounds Number identified components Total concentration of volatile compounds (TVOC) Number of components included in TVOC (conc. > 0,1 $\hat{I}^{1/4}$ g m-3) Sample received Samples analysed USI-2 Furnace house Id 427 9 -16 June 2017 Concentration Toluene-equivalents ($\hat{I}^{1/4}$ g m-3) 39,0 39,0 32,4 28,6 28,2 19,1 18,6 15,4 14,8 14,5 13,3 13,0 13,0 12,7 12,6 12,5 12,4 11,9 10,7 10,3 10,2 9,5 9,2 8,4 8,1 7,8 7,6 7,1 7,0 6,8 6,7 6,5 6,4 6,4 6,1 6,1 5,5 5,2 5,2 CAS no 91-20-3 95-47-6 000083-32-9 91-57-6 000629-78-7 90-12-0 629-59-4 629-50-5 544-76-3 629-62-9 112-40-3 000108-88-3 124-19-6 108-95-2 000259-79-0 000582-16-1 000581-40-8 000593-45-3 122-99-6 100-52-7 1120-21-4 92-52-4 106-42-3 629-92-5 124-18-5 575-43-9 556-67-2 000575-41-7 18435-22-8 98-86-2 003333-13-9 003910-35-8 001680-51-9 71-43-2 013287-24-6 1560-96-9 13475-82-6 000085-01-8 000071-36-3 39 215 507,7 858,9 16. June 2017 6.August.2017 11 Table 5 VOC from sample taken inside the furnace house Sampling site Sample id/tube id Sampling period Component Nonadecane Naphthalene, 1,2,3,4-tetrahydro-5-methyl- octamethyl cyclotetrasiloxane (D4) Octadecane Naphthalene, 1-methyl- Biphenyl Naphthalene, 1,2,3,4-tetrahydro-1,4-dimethyl- USI-2 Furnace house Id 142 16-23 June 2017 Concentration Toluene-equivalents ($\hat{I}^{1/4}$ g m-3) CAS no 000629-92-5 002809-64-5 556-67-2 000593-45-3 000090-12-0 000092-52-4 004175-54-6 100-52-7 000091-20-3 000643-93-6 25117-24-2 000095-48-7 000581-40-8 98-86-2 000581-42-0 000091-57-6 106-42-3 001560-89-0 1120-21-4 108-88-3 4292-92-6 000581-40-8 1560-97-0 544-76-3 000629-78-7 629-62-9 000083-32-9 000629-50-5 000582-16-1 71-43-2 80-57-9 108-95-2 112-40-3 629-59-4 95-47-6 1560-96-9 000259-79-0 NILU report 35/2017 benzaldehyde Naphthalene 1,1'-Biphenyl, 3-methyl- 4-methyltetradecane Phenol, 2-methyl- Naphthalene, 2,3-dimethyl- acetophenone Naphthalene, 2,6-dimethyl- Naphthalene, 2-methyl- p-and m- Xylene (1,4 og 1,3 Heptadecane, 2-methyl- undecane toluene pentylcyclohexane Naphthalene, 2,3-dimethyl- 2-methyldodecane hexadecane Heptadecane pentadecane Acenaphthene Tridecane Naphthalene, 2,7-dimethyl- benzene dimethylbenzene) 81,0 45,0 38,8 35,6 29,2 25,4 24,9 24,8 24,7 23,4 18,9 18,3 15,8 15,7 13,6 13,3 12,2 11,8 11,7 11,6 11,5 11,2 10,5 9,8 9,8 9,6 9,5 9,3 8,8 8,7 8,6 8,3 8,0 7,4 7,4 7,3 7,1 648,5 1076,6 29 June 2017 6 August 2017 4,6,6-trimethyl-bicyclo[3.1.1]hept-3-en-2-one

(verbenone) phenol dodecane tetradecane o-xylene (1,2-dimethylbenzene) 2-methyltridecane Biphenylene Total concentration of identified compounds Number identified components Total concentration of volatile compounds (TVOC) Number of components included in TVOC (conc. > 0,1 µg m⁻³) Sample received Sample analysed 37 209 12 4.3 Emissions within the baghouse Inside the Baghouse two samples were taken over the periods 21 May to 9 June and 16 June to 23 June. The sampling sites are shown in the pictures following the report. 4.4 Results and discussion The samples taken inside the baghouse are showing high concentrations of Phenyl maleic anhydride (cas nr 36122-35-7). This compound should stay as a solid until its melting point at 160°C. So very little of this compound should be airborne at temperatures below 100°C. The fact that the concentration in the gas phase is so high is pointing towards a much higher overall concentration since most of the compound will be particle bound or as crystals. There are other anhydrides in the sample like Phthalic anhydride (cas nr 85-44-9) pointing to the fact that anhydrides could form during the process. In both samples benzoic acid and acetophenone are among the compounds with highest concentrations both can be formed as a sampling artefact when Tenax is exposed to both high temperatures and high concentrations of oxidants like ozone. But both can also be formed by oxidation of aromatic compounds - which are definitely in the gases from the furnace house and ozone or other oxidants. Like in the furnace house the overall concentrations are low 600 and 1300 µg/m³. The inflow of naphthalenes, PAHs and hydrocarbons from the furnace house is mirrored within the sample composition. Also here the same argumentation for both the odour potential and dilution towards the vicinity of the factory is valid. Anhydrides are irritants to skin, eyes and the respiratory system. The high boiling point favours transport in the particle phase. We recommend to follow up the presence of anhydrides in both emissions and deposition in the surrounding areas. Using methods especially suited for the sampling and analysis of those compounds.

4.5 Phenylmaleic anhydride Written by NILU's toxicologist, Dr. Espen Mariussen There is very little information available about health effects and toxicity of phenylmaleic anhydride. We have not been able to find any information about the compound in the scientific literature by search on Google, PubMed or Web of Knowledge. The compound can be purchased from commercial suppliers, from which safety data sheet (SDS) has been obtained. According to the SDS from one of the distributors (Fisher scientific) the chemical is considered hazardous by the 2012 OSHA Hazard Communication Standard (29 CFR 1910.1200). According to Globally Harmonized System of Classification and Labelling of Chemicals (GHS), the chemical has a relatively low acute toxicity and defined as a category 4 chemical. A category 4 chemical has estimated oral lethal concentration of 300-2000 mg/kg body weight. As gas, the chemical is presumed to be lethal at 2500-5000 ppm, and between 10 and 20 mg/l as vapour and between 1 and 5 mg/l as dust/mist. The chemical is categorized as a skin and eye irritant, which by definition is a chemical, which is not corrosive, but which 13 NILU report 35/2017 causes a reversible inflammatory effect on living tissue by chemical action at the site of contact. The respiratory system is considered the main target organ. According to the classification criteria of GSH for specific target organ toxicity (single exposure) the chemical is a category 3 chemical, which is defined as a chemical that following a single acute exposure temporarily may cause narcotic effects such as dizziness and drowsiness, and respiratory tract irritation, such as sore throat and cough. 14 NILU report 35/2017 Table 6 VOC from sample taken inside the baghouse

Sampling site	Sample id/tube id	Sampling period	Component
			Phenylmaleic anhydride
			acetophenone
			Phthalic anhydride
			benzoic acid
			Dibenzofuran
			naphthalene
			Benzoylformic acid
			benzonitrile
			Benzeneacetonitrile, alpha oxo
			Anthracene
			benzaldehyde
			Biphenyl
			phenol
			sulfur dioxide
			3-phenyl-2-propenal
			Diphenyl ethanedione
			1,2-Naphthalenedione
			Phenol, 2-nitro-
			tridecane
			1H-Indene,
			2,3-dihydro-1,1,3-trimethyl-3-phenyl-
			Biphenylene
			1H-Indene-1,3(2H)-dione
			1,3-Isobenzofurandione,
			4-methyl-
			Diethyl Phthalate
			acetic acid
			tetradecane
			octamethyl cyclotetrasiloxane (D4)
			9,10-Phenanthrenedione
			4-Methylphthalic anhydride
			Phenol,
			4-methyl-2-nitro-
			1,4-Naphthalenedione

Total concentration of identified compounds Number identified components Total concentration of volatile compounds (TVOC) Number of components

included in TVOC (conc. > 0,1 $\hat{I}^1/4g m^{-3}$) Sample received Sample analysed USI-3 Baghouse inside Id 724 21 May-09 June 2017 Concentration Toluene-equivalents ($\hat{I}^1/4g m^{-3}$) 187,6 60,6 45,7 31,0 17,2 17,0 15,7 15,5 13,3 11,6 11,5 10,4 7,9 7,2 6,8 4,8 4,5 4,4 4,3 3,8 3,4 3,4 3,2 2,8 2,8 2,7 1,9 1,9 1,8 1,7 1,6 CAS no 036122-35-7 98-86-2 000085-44-9 65-85-0 000132-64-9 91-20-3 000611-73-4 100-47-0 613-90-1 000120-12-7 100-52-7 000092-52-4 108-95-2 7446-09-5 104-55-2 134-81-6 524-42-5 000088-75-5 629-50-5 003910-35-8 000259-79-0 000606-23-5 004792-30-7 000084-66-2 64-19-7 629-59-4 556-67-2 000084-11-7 019438-61-0 000119-33-5 000130-15-4 NILU report 35/2017 31 182 508,0 608,0 16 June 2017 19 August 2017 15 Table 7 VOC from sample taken inside the baghouse Sampling site Sample id/tube id Sampling period Component Benzoic acid Phenylmaleic anhydride Acetophenone 119,9 NILU report 35/2017 USI-3 Baghouse, inside Id 63 16 -23 June 2017 Concentration Toluene-equivalents ($\hat{I}^1/4g m^{-3}$) CAS no 000065-85-0 036122-35-7 000098-86-2 000100-47-0 000091-20-3 000085-44-9 000100-52-7 613-90-1 7446-09-5 000541-05-9 000084-66-2 000088-75-5 000071-36-3 000134-81-6 000064-19-7 000108-95-2 000132-64-9 000124-07-2 000556-67-2 000700-38-9 000092-52-4 000629-50-5 002243-27-8 000085-01-8 000108-88-3 000112-40-3 001120-21-4 591-76-4 000134-81-6 541-02-6 353,4 144,0 Benzonitrile Naphthalene Phthalic anhydride Benzaldehyde Benzeneacetonitrile, alpha oxo sulfur dioxide Cyclotrisiloxane, hexamethyl- Diethyl Phthalate Phenol, 2-nitro- 1-Butanol Ethanedione, diphenyl- Acetic acid Phenol Dibenzofuran Octanoic acid Cyclotetrasiloxane, octamethyl- 5-Methyl-2-nitrophenol Biphenyl Tridecane Nonanenitrile Phenanthrene Toluene Dodecane Undecane 2-methylhexane Ethanedione, diphenyl- decamethyl cyclopentasiloxane (D5) Total concentration of identified compounds Number identified components Total concentration of volatile compounds (TVOC) Number of components included in TVOC (conc. > 0,1 $\hat{I}^1/4g m^{-3}$) Sample received Sample analysed 30 187 48,7 42,6 40,7 26,6 21,6 19,2 16,3 16,2 14,5 13,8 13,6 13,3 11,5 10,8 9,7 9,5 8,3 8,2 7,9 7,0 5,7 5,4 5,2 5,0 5,0 4,5 4,5 1012,7 1297,1 29 June 2017 06 August 2017 16 4.6 Emissions from outside the baghouse On the outside of the baghouse three samples were taken over the periods 21 May to 9 June , 9 June to 16h June and 16 June to 23d June. The samples were taken on Tenax tubes based on diffusive sampling 4.7 Results and discussion The results are an average concentration over the whole sampling period of 19 days for the first period and one week for the others. The samples are taken outside â meant to cover diffusive emissions from leaks and vents of the factory. Meteorological conditions like wind speed would have a major influence on the total concentrations taken up by the passive samplers. The concentrations are lower, as expected. The samples do show the same compounds as the emissions from the baghouse and furnace house. The concentrations of phenylmaleic anhydride are 4.4 $\hat{I}^1/4g/m^3$, 4.5 $\hat{I}^1/4g/m^3$ and 2.5 $\hat{I}^1/4g/m^3$. It should be noticed - that already here so close to the main emission vents from the baghouse - the dilution is already quite big and there are no compounds showing a concentration level higher than 20 $\hat{I}^1/4g/m^3$. 17 NILU report 35/2017 Table 8 VOC from sample taken outside the baghouse Sampling site Sample id/tube id Sampling period Component acetophenone benzaldehyde hexamethyl cyclotrisiloxane (D3) octamethyl cyclotetrasiloxane (D4) phenol Phenol, 3-methyl- pentadecane naphthalene heptadecane Sulfur dioxide toluene acetic acid Phenylmaleic anhydride hexadecane p-and m- Xylene (1,4 og 1,3 dimethylbenzene) 2-methylnaphthalene decane 2-furancarboxaldehyde 2,2,4,6,6-pentamethyl heptane benzonitrile dodecamethyl cyclohexasiloxane (D6) tridecane Benzene 1-methylnaphthalene Phenol, 4-methyl-2-nitro- 1,2-propanediol decamethyl cyclopentasiloxane (D5) octadecane undecane Naphthalene, 1,6-dimethyl- 2-phenoxyetha nol nonane 1,2,4-trimethylbenzene dodecane o-xylene (1,2-dimethylbenzene) Total concentration of identified compounds Number identified components Total concentration of volatile compounds (TVOC) Number of components included in TVOC (conc. > 0,1 $\hat{I}^1/4g m^{-3}$) Sample received Sample analysed USI-1 Baghouse, outside Id 221 21 may-9 June 2017 Concentration Toluene-equivalents ($\hat{I}^1/4g m^{-3}$) CAS no 98-86-2 100-52-7 541-05-9 556-67-2 108-95-2 000108-39-4 629-62-9 91-20-3 629-78-7 7446-09-5 108-88-3 64-19-7 036122-35-7 544-76-3 106-42-3 91-57-6 124-18-5 98-01-1 13475-82-6 100-47-0 540-97-6 629-50-5 000071-43-2 90-12-0 000119-33-5 57-55-6 541-02-6 593-45-3 1120-21-4 000575-43-9 122-99-6 111-84-2 95-63-6 112-40-3 95-47-6 NILU report

35/2017 12,8 12,4 9,5 9,0 8,4 6,9 6,6 6,1 5,1 4,7 4,6 4,5 4,4 4,2 4,1 3,6 3,5 3,3 3,3 3,2 3,1 3,0 2,8 2,6 2,6 2,6 2,6 2,5 2,4 2,3 2,2 2,2 2,1 2,1 2,1 35 209 157,5 277,8 16 June 2017 19 June 2017 18

Table 9 VOC from sample taken inside the baghouse Sampling site Sample id/tube id Sampling period Component Phenol, 2-nitro- hexanoic acid Phenol Naphthalene, 2-methyl- tetradecane hexamethyl cyclotrisiloxane (D3) Phenol, 3-methyl- Nonanal p-and m- Xylene (1,4 og 1,3 dimethylbenzene) Dibenzofuran nonane 2,4-dimethylheptane Toluene Ethanol, 2-phenoxy- Isonitrosoacetophenone Benzene Benzaldehyde Diethyl Phthalate Heptane, 2,2,4,6,6-pentamethyl- Acetic acid decamethyl cyclopentasiloxane (D5) n-Hexane Nonanoic acid octamethyl cyclotetrasiloxane (D4) Phenylmaleic anhydride Pentadecane Phthalic anhydride Benzaldehyde, 2-hydroxy- 1-Phenoxypropan-2-ol Phenanthrene Naphthalene Butanoic acid Decane Acetophenone Furfural 1-Butanol Total concentration of identified compounds Number identified components Total concentration of volatile compounds (TVOC) Number of components included in TVOC (conc. > 0,1 $\hat{1}/4g\ m^{-3}$) Sample received Sample analysed USI-1 Baghouse, outside Id 139 9.-16.June 2017 Concentration Toluene-equivalents ($\hat{1}/4g\ m^{-3}$) CAS no NILU report 35/2017 36 199 17,9 000088-75-5 16,6 142-62-1 14,5 000108-95-2 13,9 000091-57-6 11,8 629-59-4 10,2 541-05-9 9,7 000108-39-4 8,6 000124-19-6 8,5 106-42-3 8,3 000132-64-9 7,7 111-84-2 7,5 2213-23-2 7,0 000108-88-3 6,8 000122-99-6 6,6 000532-54-7 6,3 000071-43-2 6,3 000100-52-7 6,0 000084-66-2 5,9 013475-82-6 5,0 000064-19-7 4,9 541-02-6 4,7 000110-54-3 4,7 112-05-0 4,5 556-67-2 4,5 036122-35-7 4,2 000629-62-9 4,1 000085-44-9 4,0 000090-02-8 3,7 000770-35-4 3,5 000085-01-8 3,2 000091-20-3 3,2 000107-92-6 3,2 000124-18-5 3,1 000098-86-2 3,1 000098-01-1 3,0 000071-36-3 246,7 528,2 29 June 2017 06 August 2017 19 Table 10 VOC from sample taken inside the baghouse Sampling site Sample id/tube id Sampling period USI-1 Baghouse, outside Id 505 16-23 June 2017 Concentration Toluene-equivalents ($\hat{1}/4g\ m^{-3}$) NILU report 35/2017 Component 1-Butanol 12,6 CAS no 000071-36-3 541-02-6 000108-95-2 108-88-3 000770-35-4 000098-86-2 111-84-2 000132-64-9 110-82-7 000088-75-5 7446-09-5 541-05-9 142-82-5 000122-99-6 36122-35-7 000120-12-7 629-62-9 2040-96-2 110-54-3 000084-66-2 000096-37-7 100-47-0 13475-82-6 95-47-6 000071-43-2 000064-19-7 000096-48-0 100-52-7 000091-20-3 000085-44-9 556-67-2 142-62-1 629-50-5 106-42-3 124-18-5 000124-19-6 6846-50-0 decamethyl cyclopentasiloxane (D5) Phenol toluene 1-Phenoxypropan-2-ol Acetophenone nonane Dibenzofuran cyclohexane Phenol, 2-nitro- sulfur dioxide hexamethyl cyclotrisiloxane (D3) heptane Ethanol, 2-phenoxy- MALEIC ANHYDRIDE, PHENYL- Anthracene pentadecane propylcyclopentane hexane Diethyl Phthalate Cyclopentane, methyl- benzonitrile 2,2,4,6,6-pentamethyl heptane o-xylene (1,2-dimethylbenzene) Benzene Acetic acid Butyrolactone benzaldehyde Naphthalene Phthalic anhydride octamethyl cyclotetrasiloxane (D4) hexanoic acid tridecane p-and m- Xylene (1,4 og 1,3 dimethylbenzene) decane Nonanal TXIB (2,2,4-Trimethyl-1,3-pentanediol diisobutyrate) Total concentration of identified compounds Number identified components Total concentration of volatile compounds (TVOC) Number of components included in TVOC (conc. > 0,1 $\hat{1}/4g\ m^{-3}$) Sample received Sample analysed 37 200 10,3 8,4 7,4 5,7 5,7 5,5 5,2 4,9 4,7 4,5 4,2 3,1 2,8 2,5 2,3 2,3 2,1 2,1 2,1 2,1 2,1 2,0 1,8 1,8 1,8 1,8 1,8 1,7 1,6 1,6 1,5 1,5 1,5 1,4 1,4 1,3 127,1 211,8 29 June 2017 06 August 2017 20 5 Literature 1- Safety data sheet Phenylmaleic anhydride, Thermo Scientific, 26th may 2017 2- OSHA (2016). US Occupational safety and health administration. Hazard Classification Guidance for Manufacturers, Importers, and Employers. OSHA 3844-02 2016. www.osha.gov. NILU report 35/2017 21 NILU report 35/2017 Figure 1 Location of samplers besides vents inside furnace house at site USI-2. Figure 2 Tenax tubes at site USI-2 22 NILU report 35/2017 Figure 3 Spectrum from sample taken inside furnace house (site USI-2) Figure 4 Sampling site USI-1, outside baghouse. The samplers are marked with red circle. 23 NILU report 35/2017 Figure 5 Tenax tubes at site USI-1, outside baghouse. Figure 6 Spectrum from sample taken at site USI-1. 24 Figure 7 Sampling site USI-3, inside baghouse. The samplers are marked with red circle. Figure 8 Spectrum from sample taken at site USI-3, inside baghouse. NILU report 35/2017 25 NILU

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Element Distribution in Silicon Refining: Thermodynamic Model and Industrial Measurements

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To establish an overview of impurity elemental distribution among silicon, slag, and gas/fume in the refining process of metallurgical grade silicon (MG-Si), an industrial measurement campaign was performed at the Elkem Salten MG-Si plant in Norway. Samples of in- and outgoing mass streams, i.e., tapped Si, flux and cooling materials, refined Si, slag, and fume, were analyzed by high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS), with respect to 62 elements. The elemental distributions were calculated and the experimental data compared with equilibrium estimations based on commercial and proprietary, published databases and carried out using the ChemSheet software. The results are discussed in terms of boiling temperatures, vapor pressures, redox potentials, and activities of the elements. These model calculations indicate a need for expanded databases with more and reliable thermodynamic data for trace elements in general and fume constituents in particular.

INTRODUCTION

Metallurgical grade silicon (MG-Si) is produced in the electric arc furnace followed by an oxidative ladle refining (OLR) step. These two process steps are illustrated in Fig. 1. The OLR is primarily aimed at removing Ca and Al from the tapped silicon and involves purging the melt with an air-oxygen mixture, preferentially oxidizing the impurities into a slag phase. Silica fume (SiO₂) will be generated at the furnace top by combustion of exhaust gas containing SiO(g). The silica from the furnace top is usually collected and sold as a product for many applications. Silica fume will also form whenever liquid silicon is in contact with oxygen, as in the OLR process. The fume is not only a source of silicon loss, but it is also harmful to the health of the workers at the silicon plant when inhaled. For that reason, the use of dust masks are mandatory in exposed areas in most silicon plants in Norway. In addition to SiO₂, the exhaust gas from the furnace contains traces of other elements originating from impurities in charge materials, electrodes, etc. The fume from the OLR process, which is one of the main sources of fugitive emissions in the plant, in contrast to the furnace exhaust gas, is often only partly vented and seldom analyzed. The production of MG-Si and other metals is regulated by strict environmental laws, which are continuously upgraded in terms of adjusting the emission limits and requiring higher accuracy in the emission reporting. It is therefore important for silicon producers to be able to account for the pathway of individual trace elements, in particular those of a toxic nature, throughout every step of the production. In this article, industrial measurements and thermodynamic considerations are used to provide an overview of the elemental distribution between phases in the silicon refining process. This information will constitute a basis for further work aimed to quantify and limit the total emission rate. In a separate publication, various sources of error and uncertainties were evaluated with respect to the industrial ability to make accurate estimations of the fugitive emissions from the silicon refining process. (Published online November 8, 2014)

Næss, Kero, Tranell, Tang, and Tveit Fig. 1. Schematic of the phases present in the furnace and ladle. The oxidation mechanism at the Si surface is also illustrated.

The Furnace Fume and the Boiling Point Model

The elemental distribution in the electric arc silicon furnace has been studied by Garcia and Myrhaug,⁸ and some of the results are illustrated in Fig. 2. A so-called "boiling-point-model" was developed by Myrhaug and Tveit⁹ for the elemental distribution in a ferrosilicon furnace to predict the trends in distribution of elements between the outgoing phases of the furnace. Although the fundamental principles of their work may be applicable to the OLR as well, there are some differences between the furnace and the ladle that may alter the behavior of certain elements. The boiling temperatures¹¹ of all elements included in this work are plotted in Fig. 3, along with the process temperature of the ladle. The operation temperature of the

furnace ($\approx 2,000^\circ\text{C}$) is considerably higher than that of the ladle ($\approx 1,500^\circ\text{C}$), which is likely to influence the volatility of elements and compounds. The reducing conditions of the furnace may also result in somewhat different elemental behavior than in the oxygen-purged ladle. According to the boiling point model,⁹ elements with boiling temperatures higher than the process temperature will preferentially stay in the condensed phase while elements with boiling temperatures below the process temperature should go off as fume or gas. This is on the condition that they are present in elemental form. For elements present as oxides or other compounds, the boiling temperature of the compound will be decisive. Elements with vapor pressure higher than Si are also likely to report preferentially to the fume.¹² The boiling temperatures presented in Fig. 3 are for the pure elements; thus, the boiling point model assumes an ideal behavior of the elements. It is, as such, a crude estimation of the pathways of the elements. The Refining Process and the Oxidation Potential Silicon from the furnace is tapped into a ladle together with a small amount of slag. The OLR treatment consists of purging a mixture of air and oxygen through the melt from a nozzle in the bottom of the ladle (see Fig. 1). The oxygen in the refining gas will react with the silicon to form silica slag at the gas bubble/melt interface via the reaction: $\text{Si} + \frac{1}{2} \text{O}_2 \rightarrow \text{SiO}_2$ (1) The silica at the bubble-silicon interface will further react with the main impurities aluminum (Al) and calcium (Ca) via the exchange reactions (1): $4\text{Al} + 3\text{SiO}_2 \rightarrow 3\text{Si} + 2\text{Al}_2\text{O}_3$ (2) $2\text{Ca} + \text{SiO}_2 \rightarrow \text{Si} + \text{CaO}$ (3) The purging of the gas stirs the melt, pushing the produced top slag toward the periphery of the ladle in the form of a ring, leaving the Si in the vortex free of slag. The slag will change composition over the refining cycle and, thus, establish equilibrium with the silicon at the silicon-slag interface. A sample of the tapped Si is collected and tested for its Al and Ca concentration. From this information, the exact amount of flux material is calculated. The flux consists of silica/quartz sand and is Element Distribution in Silicon Refining: Thermodynamic Model and Industrial Measurements 2345 Fig. 2. Distribution of elements in the mass flows out of the furnace: tapped Si, silica fume from the furnace top, and exhaust gas. The distribution coefficients for the tapped silicon and the condensed silica fume are displayed in each column, at the base and the top, respectively. All values are taken from Garcia and Myrhaug.⁸ Fig. 3. The melting and boiling temperatures of the elements plotted with the process temperature of the ladle ($\approx 1,500^\circ\text{C}$). added to get the desired slag composition and, thus, the preferred silicon composition. Cooling material is added to adjust the temperature of the product before casting, and the amount is determined by monitoring the temperature of the melt. The cooling material consists mainly of fines from the crushing of the Si product; thus, it will have approximately the same composition as the refined product. When the refining is finished, which it usually is by the time the ladle is full, the Si is cast and the remaining slag is removed from the ladle. A schematic overview of the phases present in the ladle is shown in Fig. 1, including the mechanism for the formation of fume. The fumes derive from the partial oxidation of silicon at the surface, resulting in formation of SiO gas. As this gas leaves the surface, it is oxidized further to become amorphous SiO₂ fume. The quantitative and qualitative measurements of the fumes as well as the characterization of fume particles with respect to particle size distribution are reported in earlier work.² In addition to silicon, other elements may also be vaporized or oxidized and, thus, follow the SiO gas to end up in the fume from the ladle. The oxidation potential of each element may be used, in combination with the boiling point of each element and their oxides, to understand the pathway through the OLR process. The relative redox potential for the element, compared with silicon/silica, and its activity coefficient in the liquid metal decides the direction of this equilibrium reaction. This information is illustrated in Fig. 4, and Eq. 4 outlines the general exchange reaction for the refining of elements from the silicon melt: $x\text{Me} + \frac{3}{4}\text{SiO}_2 \rightarrow \text{Me}_2\text{O} + \frac{3}{4}\text{Si}$ (4) where Me represents an arbitrary impurity element in Si and a bar under the element abbreviation indicates its elemental presence in the silicon melt. In an ideal description of the system, elements with higher Gibbs free energy of oxidation than silicon have two possible paths: silicon or fume. The elements with 2346 NÅ|ss, Kero, Tranell, Tang, and Tveit lower Gibbs free energy of oxide formation will oxidize and report to the slag. With deviation from ideality, elemental behaviors will be altered. Although many

of the binary Si-Me alloy systems are thermodynamically described, the element distribution among a complex slag, a silicon alloy, and fume has, to date, not been measured and no attempt to predict it has been made.^{3,9,13-15} In the present study, the elemental distribution of this complex system is experimentally determined and compared with previously available data through the use of modern databases. METHOD Industrial Sampling and Analysis A comprehensive industrial measurement campaign was performed on a 35-MW furnace at the Elkem Salten MG-Si plant in Norway. The furnace produces 25,000 tons of high-silicon alloy per year, and it is one of three furnaces at the plant. Samples of silicon, slag, and fume were collected, as illustrated in Fig. 5, from eight different refining ladles with a standard purge gas mixture and flow rate conditions during 3 days. At the time of sampling, the temperature in the Si was in the range of 1,446–1,677°C. Samples from the tapped Si, as tapped into the ladle, were taken from the tapping jet. A sample of the fully refined Si was collected just before casting. Slag samples were gathered from the bottom of the ladle, from the side (freeze lining), and from the top layer. Fume samples were collected with a “cold finger” (a water-cooled copper tube) placed in the exhaust gas channel during tapping. Samples, sampling times, and conditions are detailed in Table I. Fig. 4. Gibbs free energy of oxidation of silicon and all the elements discussed in this article. The energies are calculated for one mole of oxygen, and the most stable oxides are used. All oxides below silicon are more easily oxidized to their corresponding oxides than silicon to silica. Fig. 5. Sketch of the sample collection procedure in the ladle. Element Distribution in Silicon Refining: Thermodynamic Model and Industrial Measurements 2347 Table I. Overview of samples taken and their respective conditions

Sample	Jet	Fume	Refined	Slag	Cooling material	Flux material	Taken when	Collected
							early in the tapping process	early in the tapping process
							Right before casting	After casting
							Three parallels from the batch	From three different bags
							T in melt (°C)	1,551–1,677
								1,446–1,506

Three parallel samples of the added cooling and flux materials were taken. The amount of added flux material varied from 0 kg to 320 kg and cooling material from 0 kg to 250 kg per ladle. A total of 105 samples of different phases and material streams were collected and analyzed by inductively coupled plasma mass spectrometry (ICP-MS) (Element2 from Thermo Electronics). The solid bulk samples were crushed to a powder and dissolved in acids prior to ICP-MS analysis. The sample preparation process is detailed elsewhere.¹⁰ All samples were analyzed by ICP-MS with respect to 62 elements, as listed in Table II. When specific elemental contamination was observed in individual samples, these elements were singled out and treated accordingly. Alas, Cu contamination was found to afflict all the fume samples taken with the “cold finger” (chips of the soft copper metal were discovered in the samples). To calculate the overall distribution of Cu, a recovery rate of 100% was assumed and any conclusions on the Cu distribution are based on this assumption. Recovery calculations have been carried out according to: Thermochemical Simulation $\%R = \frac{m_{i,out}}{m_{i,in}} \times 100$ where $\%R_i$ is the recovery in %, and $m_{i,out}$ and $m_{i,in}$ are the total masses of element i going out of and into the ladle, respectively. Outgoing mass flow is the sum of the refined Si, the slag, and the fume. Ingoing mass flow is the sum of the tapped Si, the cooling material, and the flux material. The experimental distribution ratio between the condensed phases (slag and silicon) was calculated for elements that could not be modeled thermochemically as a result of a lack of data in databases, according to: Equilibrium calculations for the distribution of 19 impurity elements in liquid silicon and gas (fume) and 17 elements in molten slag, as well as their stoichiometric pure compounds, have been carried out using the ChemSheet Add-In Gibbs energy minimizer in the Microsoft Excel (Microsoft Corporation, Redmond, WA) spreadsheet.¹⁶ A proprietary thermochemical database^{17,18} has been developed for this purpose, and the 19 elements chosen for the model are the best described elements in the system, with the most reliable thermodynamic data. Thermodynamic descriptions of liquid Si-based Ag-Al-B-Ca-Cd-Co-Cr-Cu-Fe-K-Mg-Mn-Na-Ni-O-P-Pb-Ti-V-Zn melts have been taken from previous work.¹⁸ Thermodynamic properties of the pure compounds were taken from the FACT pure substance database.¹⁹ The cell model has been selected for the description of the non-ideal behavior of molten oxide phase containing P₂O₅-SiO₂-TiO₂-Al₂O₃-B₂O₃-Cr₂O₃-

Ti₂O₃-CaO-FeO-MgO-MnO-NiO-PbO-ZnO-Ag₂O- Cu₂O-K₂O-Na₂O. The model parameters for the P₂O₅-SiO₂-TiO₂-Al₂O₃-B₂O₃-Cr₂O₃-Ti₂O₃-CaO-FeO- MgO-MnO subsystem were taken from the publication of Gaye et al.²⁰ For those of B₂O₃, NiO, PbO, ZnO, Ag₂O, Cu₂O, K₂O and Na₂O in the molten slag phase, the model parameters were estimated from proprietary database¹⁷ in order to estimate the distribution. Since these impurities in liquid silicon are in the range of dilute (1%), such a treatment will not bring significant error in equilibrium calculations. Measured elemental concentrations are presented in Table III, and the measured values for the tapped silicon were used for the simulations. The model calculations have been carried out under the following assumptions: (5) $L_{exp} \approx w_{El} \frac{\delta^{slag}}{\delta^{Si}}$ (6) No concentration gradients exist in the liquid silicon and slag phases. Reactions between metal/slag/gas go completely to equilibrium. The composition of the tapped silicon is constant. The measured average refining temperatures are used in the simulations. The oxidation of silicon metal by the bottom air-blowing and on the surface of liquid metal during the ladle refining are accounted for in the simulations. *i*, in where L_{exp} is the experimental distribution ratio, w_{El} is the weight percent of the element in the refined silicon alloy, and w_{ElOx} is the weight percent of the element oxide in the slag phase.

2348 N₂, Kero, Tranell, Tang, and Tveit Table II. Concentration of elements, ordered by boiling point, in the outgoing phases of the ladle

Element	Fume (ppm)	Slag (ppm)	Refined silicon (ppm)																																																																																																																																																																																																												
Si	1.9 × 10 ³	6.7 × 10 ⁶	2.1																																																																																																																																																																																																												
W	Ta																																																																																																																																																																																																														
Th	Nb	Mo	Hf	Ir	Os	Zr	<500	10 ¹⁰⁰	100 ⁵⁰⁰	U	<5	0.1 ⁵	1 ⁵	B	10 ⁵⁰	10 ⁵⁰																																																																																																																																																																																															
10 ⁵⁰	Pt	b	b	b	<5	<0.5	<5	<5	<10	0.1 ^{0.5}	0.5 ⁵	1 ⁵	1 ⁵	1 ⁵	0.5 ⁵	0.1 ^{0.5}																																																																																																																																																																																															
1 ⁵	1 ⁵	1 ⁵	1 ⁵	0.1 ⁵	<5	Pr	La	Ce	V	Lu	Y	Ti	Tb	Nd	Co	Ni	Er	Fe	Au	Sc	Ge	Ho	Cr	Sn																																																																																																																																																																																							
Dy	Cu	Al	Be	Ga	Ag	1 ⁵⁰⁰	b	b	1.4	Mn	1 ⁵⁰⁰	b	0.01 ^{0.5}	10 ^{5,000}	0.1 ⁵	<5	0.1 ⁵	1 ⁵	<10	0.5 ¹⁰	5 ⁵⁰	<50	1 ⁵⁰	<50	5 ⁵⁰	10 ⁵⁰	10 ⁵⁰	<0.5	0.01 ¹	0.01 ^{0.1}	<10	<1,000	<0.5	<10	<10	1 ⁵⁰	<5	<105	0.001 ^{0.01}	<5	0.1 ⁵	<0.5	5 ⁵⁰	<5	<5	100 ^{1,000}	1,000 ¹⁰⁴	0.01 ⁵	0.1 ⁵	5 ⁵⁰⁰	0.001 ^{0.01}	<0.5	0.01 ^{0.5}	500 ^{5,000}	<50	100 ^{1,000}	0.1 ^{0.5}	0.5 ¹⁰	1 ¹⁰	1 ⁵⁰	0.1 ⁵	1,000 ⁵	10 ⁴	0.001 ^{0.005}	0.5 ⁵	0.1 ⁵	0.1 ¹	10 ¹⁰⁰	0.01 ^{0.5}	0.1 ⁵	5 ⁵⁰	5,000 ⁵	10 ⁴	1 ⁵⁰	0.05 ^{0.5}	0.5 ¹⁰	500 ^{1,000}	0.1 ^{0.5}	5 ⁵⁰	5 ¹⁰	10 ⁵⁰	0.1 ⁵	10 ⁴	5 ¹⁰⁴	0.001 ^{0.005}	1 ⁵	1 ⁵	0.1 ^{0.5}	10 ¹⁰⁰	0.1 ^{0.5}	0.5 ⁵	10 ⁵⁰	1,000 ^{5,000}	0.01 ^{0.5}	0.1 ¹	In	Tm	Ba	Sm	Pb	Sb	Bi	Ca	Tl	<0.5	b	b	<500	<5	0.5 ⁵⁰	<50	<1	0.01 ^{0.1}	b	5 ¹⁰⁰	5 ⁵⁰	0.05 ¹	100 ^{5,000}	10 ⁵⁰⁰	100 ¹⁰⁰⁰	0.1 ⁵	0.1 ¹	5 ¹⁰⁰	1 ¹⁰	0.28	3.7 × 10 ⁴	5.7 × 10 ⁵	2.5 × 10 ⁵	0.013	2.9 × 10 ⁷	7.7 × 10 ⁴	1.8 × 10 ³	1.5	6.7 × 10 ⁴	5.5	0.72	0.45	1.4	50 ¹⁰⁰	4.6 × 10 ³	b	3.9	0.05 ^{0.5}	<5	0.5 ⁵	0.01 ^{0.5}	29	0.01 ^{0.1}	4.4	b	26	10 ¹⁰⁰	4.1 × 10 ³	1 ⁵⁰	0.05 ^{0.5}	0.017	<5 ¹⁰⁴	10 ^{1,000}	<5	Sr	Li	Yb	Mg	Zn	Na	Cd	<50	b	b	0.73	K	500 ^{5,000}	<1,000	b	510	Rb	1 ⁵⁰	<5	b	Se	0.05 ⁵	b	b	Cs	b	b	b	As	0.1 ⁵	0.1 ^{0.5}	0.1 ^{0.5}	4.4	S	b	b	b	0.25	Hg	b	b	b	P	<1,000	5 ⁵⁰	10 ¹⁰⁰	3.1	a

Slag values are the averages of three slag phases. Activity coefficients are from the literature¹⁶ at 1,600 °C, and there is an assumed dilute solution. Elements included in the thermochemical model are written in *Italic*. Concentration is lower than the IDL.

<10 1¹⁰ 1.9 <500 b 0.018

Element Distribution in Silicon Refining: Thermodynamic Model and Industrial Measurements²³⁴⁹ ChemSage simulations were used to calculate the amount of O₂ in the OLR process. The simulations indicate that the total amount of oxygen is much higher than the O₂ introduced by bottom blowing can supply. The surface oxidation in ambient air is clearly an important source of oxygen. The element distribution among the fume, silicon, and slag phases were calculated using the spreadsheet program with the basic input parameters presented in Table III.

RESULTS AND DISCUSSION The activity coefficients of the elements in a dilute, binary, liquid silicon alloy are given in Table II, along with the measured concentration ranges of each element in the refined silicon, the slag, and the fume phases. The concentration values given in Table II are calculated minimum and maximum values; based on all sources of error from sampling to ICP-MS analysis. The sources of error, combined errors, and their calculations are discussed in detail in a separate publication.¹⁰ The ICP-MS data for some elements had large analytical errors

compared with the majority of elements.¹⁰ As a result of these errors, the numerical evaluation of the data for these elements would not be reliable and they will only be discussed in a limited manner. Two types of analytical errors were used to separate reliable from less reliable data: the instrumental detection limit (IDL) and the relative standard deviation (RSD) from the ICP-MS analysis. The elements with less reliable data, i.e., large analytical errors, were either present in concentrations below the IDL or had an RSD of the analysis values larger than 10%. In fact, most elements in this category were affected by both of these errors. A recovery interval was calculated for all 62 elements in this study using the concentration interval limits in the mass flows into and out of the ladle. For all elements, the recovery interval included 100%. Figures 6 and 7 show the distribution of the elements into and out of the ladle, respectively. The distribution is given in wt.%. Note that the mass of the fume is much smaller than the mass of the condensed phases in Fig. 7. When comparing with Fig. 2, please note that the raw Si from the furnace is the tapped Si going into the ladle. The Ladle Fume An overview of the distribution of elements in the ingoing and outgoing material flows are found in Figs. 6 and 7. It can be observed that, as predicted by the boiling point model, most elements are found in the condensed phases but many of the elements that are expected to go to the fume also remain in the melt. Only Pb, Mg, and Zn are predominant in the fume. However, when interpreting the figure, it should be kept in mind that the distribution values in the figures are calculated by mass and the masses of the slag and refined silicon are very large compared with the mass of the fume. Also, the amount of fume is difficult to estimate with high accuracy and hence has a larger measurement error.¹⁰ Table III. Input parameters thermochemical model

Parameter (unit)	Value
Total tapped Si (kg)	6,900
Fine Si addition (kg)	100
Flux addition (kg)	215
Gas rate (Nm ³ /min) ^a	3.7
Tapping time (min)	120
Gas-blowing time (min)	130

^aIncluding bottom blowing and surface reaction. Fig. 6. Distribution of elements in the mass flows into the refining ladle: tapped Si, the cooling material, and the flux material. The distribution fractions of the tapped silicon are included at the base of each column. 2350 NÅ_lss, Kero, Tranell, Tang, and Tveit Fig. 7. Distribution of elements in the mass flows out of the refining ladle: refined Si, the slag, and the fume. The distribution fractions for the refined silicon and the slag are displayed in each column, at the base and at the top, respectively. The distribution is given in mass%. Please note that the mass of the fume is much smaller than the mass of the condensed phases. Fig. 8. Experimental distribution ratio between the condensed phases (filled circle) compared with the relative Gibbs free energy of oxidation of the elements that could not be modeled. Note the logarithmic scale on the right-hand side. If the fume concentrations in Table II are interpreted in combination with Figs. 3 and 7, the results confirm that most elements expected to be in the fume have relatively high measured concentrations in the fume. Li, Sr, Ca, and Yb do not, however, primarily go to the fume as may be expected by their low boiling points. These elements form stable oxides and their oxides have higher boiling points; therefore they report to slag to a large extent. Cu, Sn, and Pb, on the other hand, are expected to remain in the melt but display high concentrations in the fume, which may be explained by their high vapor pressures and positive deviation from ideality (Sn, Pb) in Si.¹² In Table II, the concentration values obtained for Bi, Se, Cd, Tl, In, and Ag have large analytical errors (IDL and RSD) in the condensed phases, but the concentrations in the fume are relatively high and the reliability of the values in the fume are therefore good. Thus, it is concluded that these elements tend to accumulate in the fume. The ideal-behavior-based boiling point model predicts this scenario for Se, Cd, and Tl, while Bi, In, and Ag are expected to stay in the condensed state. Bi, Ag, and In have, however, higher vapor pressures than Si at 1,500Å°C and show positive deviation from ideality.¹² Element Distribution in Silicon Refining: Thermodynamic Model and Industrial Measurements 2351

Fig. 9. Comparison of modeled and experimental concentrations of 19 elements in the molten, refined Si product. Note the logarithmic y-axis. Fig. 10. Comparison of modeled and experimental concentrations of 17 elements in the slag phase. Note the broken, logarithmic y-axis. The results for elements with large analytical errors in all outgoing phases are inconclusive; these are Ir, Pt, S, Hg, and Cs. (A more detailed discussion on these errors can be found in a separate publication.¹⁰) These elements tend to be removed from the silicon phase in the furnace via the exhaust gas and

silica fume,⁸ and their concentrations are too low to detect in the ladle. These elements have high vapor pressure¹² and are therefore likely to vaporize from the ladle as well. Elements with similar vapor pressure (higher than Si at 1,500°C) and furnace behavior (they typically vaporize) that are detectable in the ladle include K, Cd, Na, Mg, Zn, and Pb. They all report to the ladle fume. Most notable differences in furnace and ladle fume are found for Li and Sr; according to Garcia and Myrhaug,⁸ they vaporize from the furnace, but in the ladle, they report to the slag instead. Some elements evaporate from both the furnace and the ladle but are reintroduced into the ladle with the flux. Therefore, Pb, Zn, and As still occur in the refined product. The Slag Refining Unless large deviations from ideality are displayed, the elemental distribution between silicon and slag is expected to depend primarily on the 2352 N_A |_{ss}, Kero, Tranell, Tang, and Tveit Fig. 11. Comparison of modeled and experimental concentrations of 19 elements in the fume (gas phase). Note the logarithmic y-axis. oxidation potential of the elements at the process temperature. Elements with a large driving force for oxidation are expected to be predominantly found in the slag. The oxidation potentials for the elements in this system are shown in Fig. 4. It can be observed from this figure in combination with Table II and Fig. 7 that most elements with more stable oxides than SiO₂ are primarily found in the slag, as expected. The tapped Si is the primary material going into the ladle, and most elements primarily found in the tapped silicon tend to remain in the silicon phase, as would be expected from the boiling point model, especially because the process temperature in the ladle is lower than in the furnace. Some of these elements respond readily to the refining treatment and transfer to a large degree to the slag phase in the ladle; these are, for example, Ca, Al, Ba, Be, Sr, Yb, and Li. Other elements respond poorly to the refining treatment and transfer only partly to the slag. Elements predominant in the refined product include Ge, Co, Ce, Ni, Ti, U, V, and Zr. As thermodynamic data for many trace elements in this complex system are not readily available, their deviation from ideality is evaluated only with respect to the oxidation potential. Figure 8 shows the relative Gibbs free energy of oxide formation for the elements that could not be modeled¹³ compared with the experimental distribution ratio between the condensed phases, L_{exp} , calculated from Eq. 6. The deviation from ideality is found for elements such as W, U, Ho, and Ba, where the distribution ratio values (black dots) are on the opposite side of the x-axis compared with the oxidation potential. Here, most elements with Gibbs free energies of oxidation higher than that of Si remain in the refined Si as expected, except Se, In, Bi, and Rb, which are primarily found in the fume. Some elements with lower Gibbs free energies of oxidation are primarily found in the slag as expected (Lu, Y, Be, Ba, etc.), whereas many remain in the silicon (Zr, U, Ce, Nd, etc.). It is likely that the activities in liquid silicon for these elements are very low. Comparison of Modeled and Experimental Results Figures 9, 10, and 11 show the concentrations of the modeled elements for the refined silicon, the slag, and the fume, respectively, compared with the experimental results. Please note the logarithmic y-axis in these figures. The model estimates that 6,629-kg Ref-Si is obtained after about 130 min of gas treatment. The modeled process produces 885- kg slag (including solid SiO₂) and 376-kg off-gas. If N₂ is excluded from the off-gas, the modeled amount of fume is 59 kg, which is close to the average of 50-kg fume measured in the plant investigation. The correlation for modeled element concentrations in the refined Si is good for most elements; 14 of 19 model concentrations fall within the corresponding experimental range and another two are in the same order of magnitude. The largest difference is found for K, for which the theoretical concentration is much lower than the experimental result. In the slag phase, however, only Ca falls within the experimental range. Al and Mg are of the experimental order of magnitude. As the experimental data reported are the average concentrations in top, bottom, and side slag observed as one phase, inhomogeneities between these phases make accurate slag/metal distribution determination a challenge. As such, data from the silicon analysis is more reliable. As such, experimental data from the silicon analysis are more reliable and the information available in databases is more extensive. Element Distribution in Silicon Refining: Thermodynamic Model and Industrial Measurements 2353 Additionally, kinetic factors, which have not been included in the current analysis, may be influencing the refining process and the system may be far away from equilibrium for several

elements. In the gas phase/fume Na and Cd are the only modeled elements with concentrations within the experimental range. The evaporation of impurities from silicon metal is likely controlled by kinetic factors, rather than by thermodynamic. Therefore, it is expected that the discrepancies between equilibrium calculations and measured values for fume are relative large. As such, intermittent sampling during a refining cycle will not give time-independent, representative flux of an element. Fume sampling at the start and end of a refining cycle may give the range of element concentrations in the fume. Nonetheless, as experimental data are the foundation for most thermochemical models available today, these results indicate a need for more and better data that can improve the databases for future modeling.

CONCLUSIONS The element distribution throughout the oxidative ladle refining of MG-Si, with respect to the mass flows into and out of the ladle, has been established. The distribution of elements between the condensed phases and fume is generally in accordance with the boiling point model. Exceptions include Bi, Ag, In, Sn, Li, Yb, and Sr, where Li, Yb, and Sr should go to the fume but are readily oxidized and therefore primarily found in the slag. Although some significant differences between the element distributions in the furnace and the ladle have been established, most elements that report to exhaust gas or silica from the furnace top are also found primarily in the fume from the ladle. Many of these elements have high vapor pressures. Elements that primarily report to the fume include Ag, Sn, Se, Cd, In, Bi, Ag Pb, Zn, and Mg. The distribution of elements between the slag and the silicon is related to the oxidation potential of the elements. Most elements with a Gibbs free energy of oxidation that is more negative than that of Si tend to be oxidized and therefore readily refined. Conversely, elements with very low concentrations and apparent activities in the ladle (such as Th, Sm, Tm, Dy, and Tb) do not oxidize and will remain in the refined product. Elements primarily found in the slag include Ca, Al, Li, Be, Ba, Sr, and Yb. To our knowledge, this publication is the first of its kind to account for the elemental distribution of both major and trace elements in the OLR process. This information is useful to the silicon producing industry as it provides a detailed description of the pathway of each element through the OLR. In particular, fume concentrations are vital to enable correct estimations of the fugitive emissions from a silicon plant. Thermochemical simulations have been performed for several elements, and the modeled concentrations are compared with measured values. The large discrepancies in the slag and fume shows that more thorough experimental data are needed for a more fundamental understanding of the thermodynamics in such a multiphase, multicomponent system. Furthermore, there is no or very limited data available for many of the trace elements, and therefore, detailed and reliable simulations are not possible until the thermodynamic databases can be expanded.

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The tapping process in silicon production

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This paper presents some of the work carried out in order to improve the tapping process in silicon production, with special focus on the environmental and the safety standards. Some of the modelling work that has been done to improve the understanding of the process is described, together with the resulting implementation to improve tapping standards.

Introduction

The tapping process has seen improvement over the past 30 years, and some important tools such as simple automated tapping equipment have been introduced. However, further developments are still required, particularly in reducing operators' exposure to diffusive emissions.

Challenges of the industrial silicon tapping process

Silicon production consists of a series of critical processes, the major ones being raw material handling, furnace operation, and refining and casting. Tapping is one of the critical processes and affects the overall process in several ways. In the tapping process, molten silicon at a temperature above 1500°C is drained from the furnace through a tap-hole, either continuously or discontinuously, using different tapping equipment. Keeping this critical process under control has several challenges:

- Good drainage of silicon from the smelting furnace is a prerequisite for stable furnace operation and optimal silicon yield. If silicon is allowed to accumulate in the furnace over time, it will react with either carbon or silicon dioxide, which in turn will disturb the furnace process and reduce the silicon yield (Schei, Tuset, and Tveit, 1998)
- Utilizing the right kind of tapping equipment is important to obtain the correct product quality. The tapping process may also have an adverse effect on the production yield and the total revenue
- The tapping area has several safety challenges. Operators are in close proximity to molten silicon, high temperatures, moving equipment, and complex logistics. The risk of burns and crush injuries is high unless preventive action is taken
- The tapping process performance affects the working environment. The tapping area is one of the largest sources of internal air pollution at the smelting plants.

Elkem has worked on the dust exposure challenges of the process through several different research programmes, both internally and in cooperation with other parties such as the Norwegian Ferroalloy Producers Research Association (FFF). Figure 1 shows the result of mapping the main dust-exposed areas at Norwegian ferroalloy smelting plants. The Norwegian Labour Inspection Authority has increased its focus on chronic obstructive pulmonary disease (COPD) with the objective of reducing dust exposure for workers in the Norwegian smelting industry (Arbeidstilsynet, 2011).

Elkem started its process dust mapping programme 1999, and the final report was presented in 2005 (Hetland, 2005). This work showed that exposure to excessive dust levels at a smelting plant over a prolonged time increases the risk of reduced lung capacity. The tapping area was found to be one of the highest risk areas. The health risks were confirmed by Johnsen (2009). These findings prompted an increased effort within Elkem to improve the working environment.

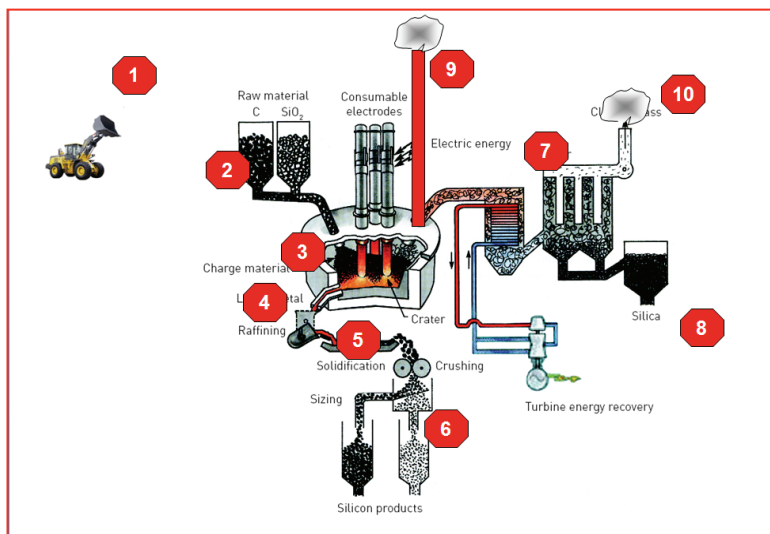


Figure 1. Main dust source areas at Norwegian ferroalloy smelting plants

As an initial step, the use of dust masks at the Elkem smelting plants became mandatory from 2005. In addition, resources were allocated to process understanding and possible technical solutions to the challenge. In 2006 the project ‘Promiljø’ was initiated (Norwegian Ferroalloy Producers Research Association, 2011), followed by the ‘Fume’ project in 2009 (Norwegian Ferroalloy Producers Research Association, 2013).

The tapping gas problem – root causes

The process gas in most reduction furnaces is mainly CO as shown in Equation [1]. Normally the furnace interior is under slight positive pressure due to the conversion of solid materials (ore or quartz plus reductants) into the liquid state and gas phase. The process gas has a much higher volume than the solid materials.



In the silicon and ferrosilicon processes this problem is exacerbated due to the existence of SiO gas, which is an inevitable product of the process. The total reaction is shown in Equation [2]–[4] Equation [3] shows the reaction that takes place in the upper part of the furnace and Equation [4] the reaction in the crater zone near the tips of the electrodes.



The SiO(g) is stable only at very high temperatures and creates the following problems in the tapping area:

- In a large industrial (ferro)silicon operation, 1 litre of solid materials is converted to around 3000–5000 litres of gas. This creates a positive pressure inside the furnace, which has been measured to be in the order of 0.01–0.07 bar. If the tap-hole condition is unfavourable this may create a tapping gas problem
- The tapping gas, consisting mainly of CO and SiO, combusts outside the tapping area, creating heat that may be harmful to operators and equipment if appropriate protection is not installed
- The combustion of the SiO gas outside the tap-hole generates amorphous SiO₂ particles that pollute the plant environment and give rise to diffusive emissions. These particles are generally smaller than 2.5 μm, making them respirable, and a fraction of these particles is also under 100 nm (Kero, Næss, and Tranell, 2013).

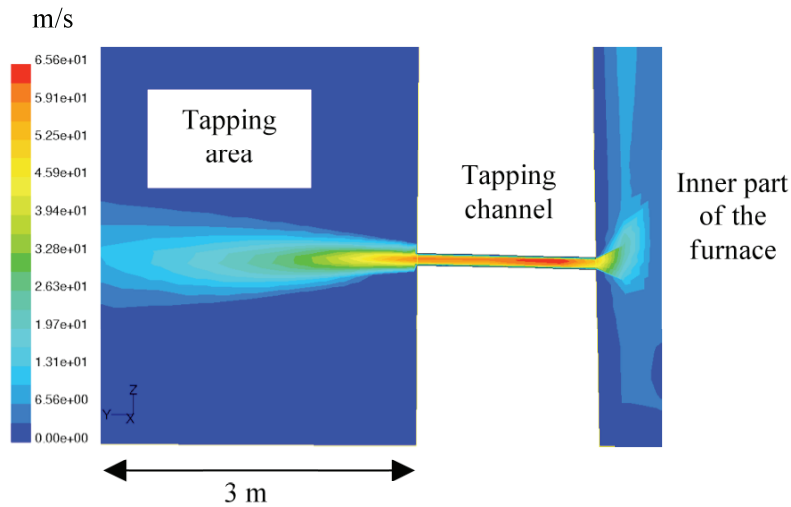


Figure 2. Velocity distribution

A computational fluid dynamics (CFD) simulation of velocity distribution of tap-hole exit gas on a scale from 0–65 m/s in the tapping region is shown in Figure 2. The jet will leave the tap-hole with a velocity of approximately 50 m/s and may become more than 3 metres long (Ravary and Laclau, 1999).

Silicon and ferrosilicon furnace multiphase flow model

To understand the problem and to find solutions a PhD project was initiated within the FFF environmental programme. The work (Kadkhodabegi 2011) included industrial measurements as well as modelling and theoretical studies. A full 3D multiphase flow model of silicon and ferrosilicon furnaces was developed. The modelling set-up is shown in Figure 3.

The model was based on CFD and fluid flows and interactions between the phases were therefore investigated. The modelling process consisted of constructing the furnace geometry, selection of the physical models regarding the assumptions and simplifications of the real system, developing user-defined sub-models, considering proper boundary conditions, and explaining the model results.

In addition to theoretical modelling, the results of industrial tests from different furnaces were used. The industrial measurements were carried out both to achieve a better understanding of phenomena in order to develop the model and to be able to validate the model.

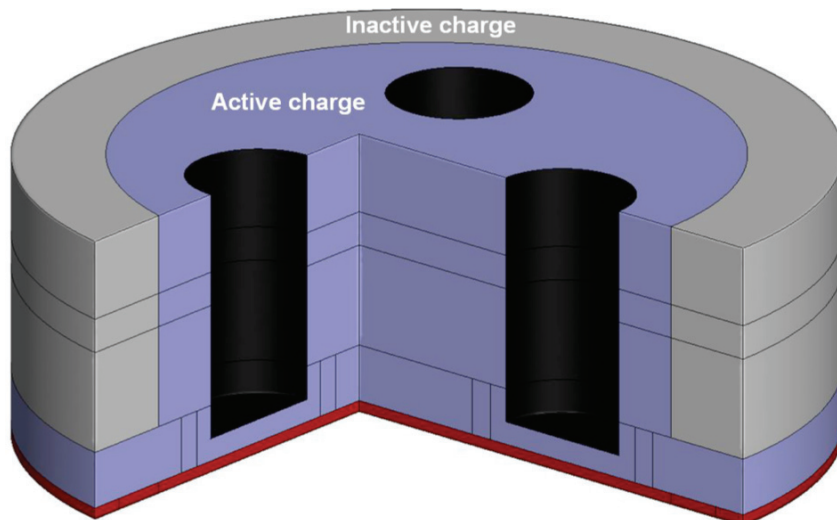


Figure 3. The 3-D dynamic model of the reaction zones, the electrodes, and the charge

The results from the modelling work are presented in Figure 4 and Figure 5. Figure 4 shows the static pressure and the silicon and gas distribution at a given time. Figure 5 shows the distribution of silicon during the whole tapping process. Note the ‘doughnut’ shape of the silicon distribution, and also that the draining of the silicon is partly along the periphery of the furnace.

The model parameters are presented in Table I.

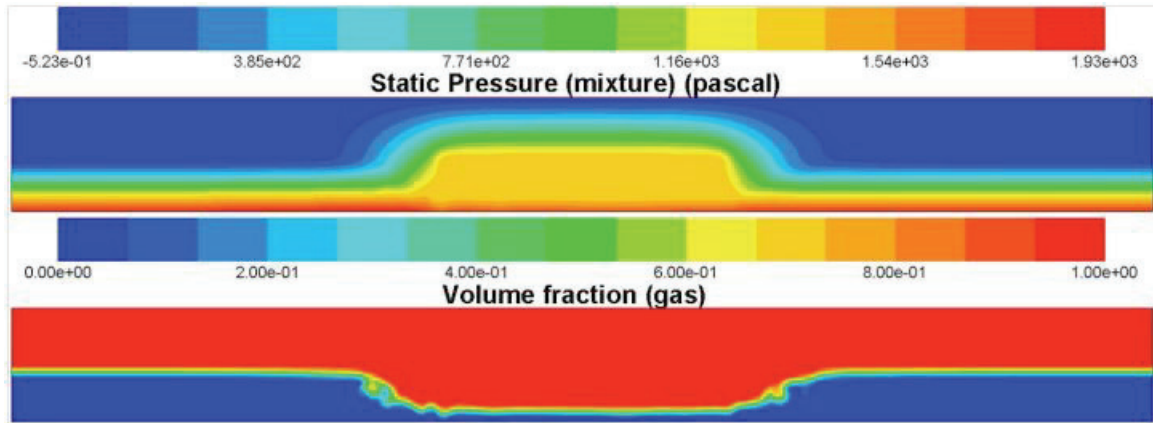


Figure 4. The calculated static pressure in the furnace above the liquid area and the volume fraction of gas. Note the clear depression of the silicon level in the centre of the furnace due to the static gas pressure



Figure 5. The ferrosilicon level during the tapping process. The gas phase is represented as yellow. The ferrosilicon (shown in red) is forced to the furnace periphery due to the static gas pressure in the furnace

Table I. Structure of the comprehensive model of tapping process in the submerged arc furnaces used for high-silicon alloy production (Kadkhodabeigi 2011)

Insight into the Structure of the CFD Model				
Parameters	Parameter Type	Detailed Parameter	Accuracy	References / Comments
Input	Geometry	Furnace diameter	High	Industrial data
		Furnace height	High	Industrial data
		Electrodes diameter	High	Industrial data
		Taphole diameter	High	Industrial data
Input	Process information	Metal production	High	Industrial data / (Schei et al. [1998])
		Gas production	High	Industrial data / (Schei et al. [1998])
		Crater pressure	Medium	Industrial tests (Ingason [1994] and Johansen et al. [1998])
		Formation of charge zones	Low	Furnace excavations (Zherdev et al. [1960]), (Otani et al. [1968]), (Schei [1967]),(Myrhaug [2003]) and (Tranell et al. [2010])
		Melts density and viscosity	High	(Rhim and Ohsaka [2000]) and (Klevan [1997])
Tuning Parameters	Physical properties	Particles size (Outer zone)	Medium	(Schei et al. [1998]) and Johansen et al. [1991]
		Particles size (Inner zone)	Tuned	Furnace excavations (Zherdev et al. [1960]), (Otani et al. [1968]), (Schei [1967]),(Myrhaug [2003]) and (Tranell et al. [2010])
		Packed bed porosity	Tuned	Furnace excavations (Zherdev et al. [1960]), (Otani et al. [1968]), (Schei [1967]),(Myrhaug [2003]) and (Tranell et al. [2010])
Output	Results of model	Tapping speed	High	Industrial tests
		Average metal height	Predicted	
		Metal pattern	Predicted	Industrial accident for leakage of melt from the furnace which confirms high metal heights close to the furnace wall
		Gas flow in the charge	Predicted	Industrial observations and (Tranell et al. [2010])

Learning outcomes of the modelling work (Ravary and Laclau, 1999; Kadkhodabeigi 2011)

The model for tapping has proved useful for the training of operators in order to improve their understanding of the behaviour of the tapping process. Of special importance is the quality of the taphole repair in order to avoid direct gas emission from the crater. The understanding of the ‘doughnut’ shape of the liquid silicon in the furnace has been useful for optimizing the tapping process and improving operational standards. The doughnut’ shape also provided a welcome explanation of some important process phenomena – why the process seems more stable and gives less SiO loss in the first 30–60 minutes after tapping. The reason for this may be explained by the reduced level of liquid silicon in the centre of the furnace and consequently little reaction with the added quartz.

The improvement work – reduced fugitive emissions in the tapping area

Theoretical principles

In 2008 Elkem Thamshavn was ready to replace the worn existing tapping fume hood with a new hood of similar design. At the same time, Elkem was focusing on the work environment and had acknowledged that fumes from tapping were the main source of pollution, emitting fugitive dust into the work environment. A new hood was therefore followed by an expectation of reduced emissions. However discussions with the engineering companies revealed that no such reduction could be guaranteed. At that point Elkem Thamshavn made the bold decision to turn down an already approved investment and focus on the theoretical principles that govern the gas emitted from the furnace through the tapping channel.

This work was organized as a joint effort between industrial workers and engineers on the one side and a PhD student and the academic approach on the other. The result was a new understanding of flow patterns and heat stresses around the flow of SiO and CO through the tapping channel.

When new knowledge is made available and spread to industrial engineers and operators, new ideas for solution are created. After some brainstorming sessions in early 2009 a new hood design (Figure 7) was suggested.

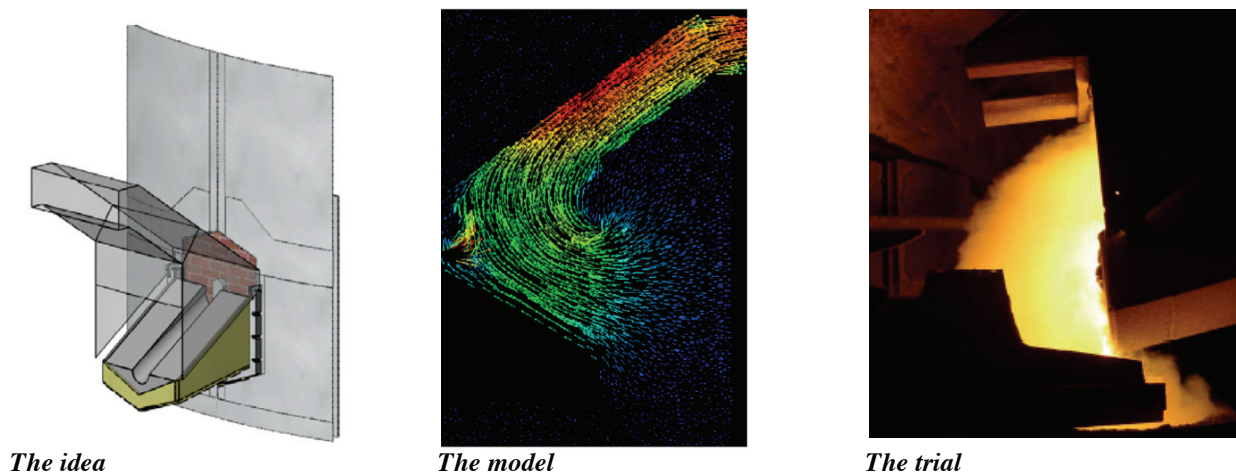


Figure 6. Development of new tapping fume extraction hood

Tapping fume extraction hood - from model to practical solution

There is, however a large step from an idea and a hypothesis based on new theoretical knowledge to a full installation on large silicon-producing submerged arc furnaces, and large steps are often associated with large risks. One of the more significant risks was that no proper mechanical solution for the hood/furnace borderline could be found. There is in addition always the possibility that assumptions made during the development of the new theory are not applicable in real life. To reduce the latter of these risks it was decided to model the suggested design in FLUENT and verify the model observations in trials at a real furnace. Through these trials the potential of the technology was demonstrated.

A set-up with modelling and verification through trials early in the development serves several purposes. First of all, the project can be stopped early if the theory turns out to be wrong, but it also increases the motivation to overcome any obstacle that lies in the way during the technical development. When the potential of the result has been demonstrated it is easier to motivate for resources both for development and for investment at a later stage.

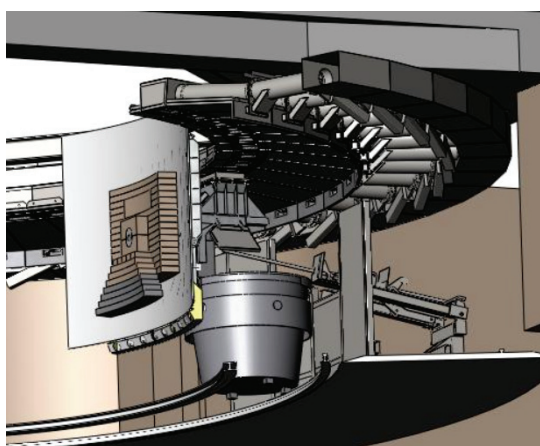


Figure 7. The industrial pilot installation

As a result of the promising trials made in the latter half of 2009 a project was organized and executed culminating in a full-scale pilot installation on a silicon furnace at Thamshavn in early 2010 (Figure 8). This installation was evaluated by SINTEF after start-up, and the improved fume collection rate was confirmed.

After three years in operation the new design has also proved to be mechanically robust, long lifetimes of parts and low maintenance costs. It also constitutes a starting point for a second-generation design which can be based on long-term observations of a full-scale pilot installation instead of the high risk involved in relying on new theoretical understanding.

The Elkem DUSTEX project

To follow up the results from Promiljø, FUME, and the Thamshavn pilot installation, and facilitate the efforts at the smelting plants to reduce dust exposure in compliance with the labour authorities' requirements, Elkem decided to establish a corporate project, 'DustEx'. The project was divided into two stages: dust mapping and risk evaluation, and a technological part with emphasis on implementation of technology and best practice for reduction of and/or capturing of process-generated dust.

Today's solution to protect employees from dust exposure relies to a great extent in the use of personal protective equipment (PPE).

The various production plants have different conditions in the problem areas, and different prerequisites for reducing dust exposure. The main dust sources have been identified, but feasible measures to reduce dust exposure to acceptable levels are incomplete.

The main focus is on developing and implementing permanent, technical solutions for fume and gas extraction. It must be emphasized that process gas also contributes to fugitive dust emissions to the external environment, and improved gas collection constitutes a positive contribution to reducing pollution in the plant vicinity.

Dust exposure mapping

In parallel with the work on technical solutions, a mapping programme for measuring personnel exposure to dust was initiated on all smelting plants. The measured dust levels form the basis for risk analysis and hence an action plan specific to each plant.

Norwegian law regulates employee dust exposure through administrative norms (ADNs) for several substances (Norwegian Labour Inspection Authority, 2013). To ensure full compliance with the norms, a separate action initiation level is set at one-quarter of the ADN. The method of measurement is a personal pump and gravimetric filter device, which is carried during an 8-hour shift. The average value from the analysis is compared to the ¼ ADN value.

ADN for total respirable dust	$\leq 5 \text{ mg/m}^3$
ADN for respirable amorphous SiO ₂	$\leq 1.5 \text{ mg/m}^3$

Also, the causes of for high intensity dust level periods will be identified, analysed, and measures taken to reduce the impact.

Development of a recommended practice (REP) for tapping fume extraction system

Efficient fume extraction during tapping is necessary for compliance with Norwegian dust exposure requirements. The ultimate goal is that all fume produced in the tapping area is captured and controlled through extraction and filter systems. To contribute to knowledge transfer and utilization of best practice, a recommended practice (REP) document was compiled based on conditions at the Elkem Thamshavn pilot installation, to ensure that the best available solutions and knowledge from our tapping fume extraction projects were available for all Elkem units.

The energy in the liquid metal and the combustion of furnace gases may result in high energy flow due to radiation and combustion heat. The tapping fume installation must be designed to be robust according to local furnace conditions.

Elkem has considerable experience with tapping fume extraction systems for its furnaces, and the purpose of the REP is:

- To provide Elkem's recommended design for tapping smoke extraction systems
- To provide the recommended method(s) and information for understanding and copying the main principles and solutions for this design.

To support compliance with this recommended practice, a tapping fume design process and quality assurance checklist is used:

- Start with Elkem Recommended Design (ERD) for tapping fume extraction.
- Check if design basis is updated according to latest completed relevant projects
- Analyse and understand ERD solution with respect to key design parameters
- Analyse relevant site for key parameters and compare to ERD
- Evaluate elements from ERD solution that can be re-used
- Develop design basis for relevant site.

Process simulation and modelling –a serious learning curve

Process engineers the last part of the 20th century and into the 21st century have been exposed to amazing developments in new technology. Knowledge of modelling, hardware development, and continual availability of improved programs and systems have revolutionized process modelling. The result of the increased possibilities has been improved concept

and design in all sectors of industry, and not least in the metallurgical sector. The direct improvement may be seen in process performance, reduced costs, improved EHS standards and more. The modelling work will also provide opportunities regarding improved understanding and learning. Today the different modelling tools may give us insight into complex fluid flow patterns and convert huge amount of calculations into easily understandable presentations.

Given the background of this wonderful improvement, one may be considered as a 'party pooper' to write about serious learning. But unfortunately the short history of the use of computer models has included some very costly learning experiences. Some of the problem seems to be inherent in the very effective communication methods that the new modelling tools may provide. Presenting the colourful results from simulations may be very convincing. A model is normally extremely simplified compared to the physical situation. In the best case, the modelling work describes the most important phenomena and the implications of the results are fully understood by all those who will utilize the results from the modelling work.

The learning outcome is that the work before the modelling is important – but maybe the most critical phase is the work necessary afterwards in order to interpret, control, and implement the modelling results as shown in Figure 9.

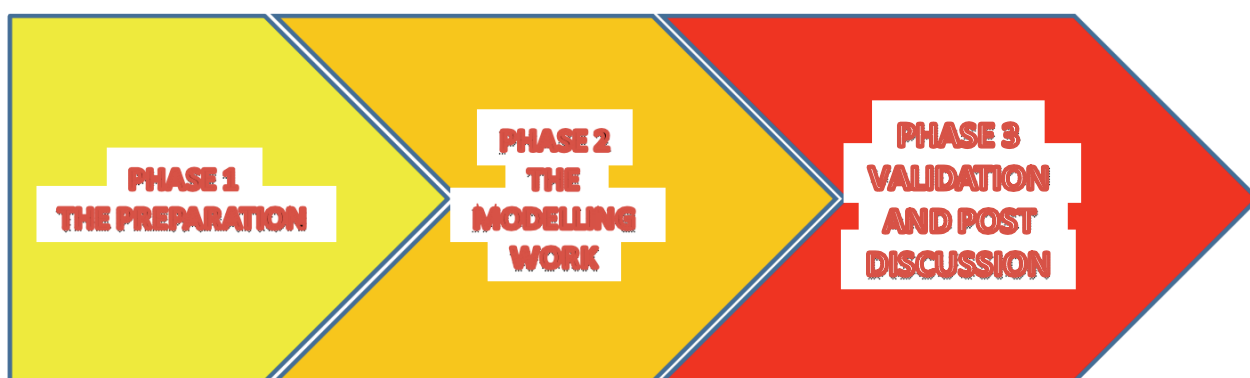


Figure 8. The main phases in the modelling process

The preparation phase (1) includes describing the real business case, setting of parameters, and the preparation for the modelling work. The important phase 3 includes both the control of the results, the interpretation, and the consequences of the results, as well as ensuring that the limitations of the modelling results are fully understood by the users.

On the positive side, a successful modelling exercise gives rise to increased understanding, and the modelling result such as data, graphs, and video presentations may be a helpful tool for design, construction, training and education of operators and engineers, and lead to a successful start-up and operation of the process.

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Worked in the Norwegian Iron and Steel plant 1974-1977. Elkem Bjoelvfossen 1977-1980. After that work at Elkem Thamshavn Plant and the Elkem Silicon Division.

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Papers

Several papers about different aspects of metallurgical processes – mainly FeSi and silicon production. Since 1998 I have been invited to give paper at the “Silicon for Silicones” conference that is held in Norway every 2 years. Main topic has been energy recovery, HES and silicon process and product items.



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I was educated as a process metallurgist at NTNU working with silicon and reaction kinetics. In 2010 I started working for Elkem at the Elkem Salten plant, working with furnace operation and microsilica production. After a period at Salten, I moved to Elkem’s technology division where my working area was slag refining for the Solar process. Now I work in Elkem’s Silicon Division’s EHS&Technology team working with post taphole process’s, such as tapping, refining and casting.



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Road mapping how to reduce the environmental emissions and energy consumption for ferrosilicon and Silicon plant Potential opportunities to reduce the environmental emissions in Metallurgical Industry a bibliography review of the process and emissions control points in Silicon and Ferrosilicon plants. M.Sc. Eng. Valdiney Domingos de Oliveira, MBA, MBB, CEng1, Dipl. Eng. Rodrigo Silva Faria, PMP, PRINCE21, Dipl. Mgr. Phillippe Machado, Env.1

1)

Viridis.iQ GmbH â von-Emmich-str.4, 78467, Konstanz, Baden Wurttemberg, Germany Abstract The world yearly production of Silicon and Ferrosilicon is estimated in 2,41 and 8,2 mio1 of tons respectively. China is responsible for 55% (Si) and 66% (FeSi) of the world production. The total amount of Submerged Arc Furnaces that could be used to produce Silicon in different grades (metallurgical for Aluminium Industry, chemical for Polysilicon and Silicones Industries, mainly) are estimate in 295 furnaces2 divided between the main producers of Silicon product along Chinese country. Based on the updated marketing information, there are 64 of that Submerged Arc Furnaces3 in the Northeast china region, which around 13 SAF3 are in normal operation by the first quarter of 2016. The Silicon and Ferrosilicon processes have some similarities in terms of equipment. Since the raw material handling system, the batching and feeding process, stocking process in the top of the furnace, the main smelting process, the tapping, refining and casting as well as the crushing, milling, grinding, screening and packaging process have different environmental emissions, qualitatively and quantitatively speaking. The target of this technical article is to provide a review of the different techniques applied in the metallurgical industry towards reducing those environmental emissions, via efficiency increase or new process and equipment implementation. Also to give a general ideal about return on investment for each separated system. The outcome of those optimization and assets improvement are the positive environmental profile plants increase that could be capitalized via the microsilica quality increase, the NOx and SOx and other gas emissions reduction and the increase of the overall plant efficiency. Although there is an analogy of this article and the direction of the 13th Five Year Plan (2016-2020), the coverage of the initiatives mentioned are applicable in any Silicon/FeSi plant worldwide; including within the general context of the efficiency drive sustainable practices to all production process through an environmental management system. Keywords: Silicon, Ferrosilicon, Submerged Arc Furnace (SAF), Off gas, NOx, SOx, microsilica, dust, environmental emissions, tapping, stocking, refining, casting, milling, environmental management system, 13th Five year Plan â PR China. 1 - Silicon and Ferrosilicon Market overview The global geographic distribution of production plants for ferrosilicon and metallurgical grade silicon is typically a function of the availability of low (and clean) electric energy, as well as the possibility of a long term contract with the local utility company; logistic access to the raw material such as the iron and silicon ore, carbon source (reducing agent called as âreductantâ) and also access to potential customers and for example, regional off-takers within the respective processing industries which use Ferrosilicon and Silicon as feedstock. In the case of Ferrosilicon, mainly Carbon and others alloys, iron casting, magnesium industry (die casting for example and primary production process) and Stainless Steel are responsible for more than 99% of FeSi usage. In the case of Silicon, the main industries are respectively Chemical Industry (Silicones and Polysilicon) and Aluminium Industry, responsible together for more than 99% too. Besides the typical oscillation into those markets (due to the economic crisis in 2008 and lower demand in 2015), the forecast for both sectors are positively evaluated by the industry worldwide. For the case of Silicon production, slightly better than Ferrosilicon: 1|Page Road mapping how to reduce the environmental emissions and energy consumption for ferrosilicon and Silicon plant Figure 1 â Global Silicon demand by application source Viridis.iQ estimates Figure 2 â Global Ferrosilicon consumption by application source Viridis.iQ estimates What is possible to note is that, in the Silicon case, the expected growth rate of 5% is higher comparing with the Ferrosilicon forecast of 3%. Is important to note that, in the case of Silicon demand by application, the Polysilicon expected demand for Silicon is driving the world Silicon demand for this higher rate comparing with Ferrosilicon, due to the new Solar Energy boom happening worldwide, with focus in developing countries such as India. If we take the expected demand for Silicon in the Polysilicon industry on 2020e (Viridis.iQ GmbH), the expected demand of Silicon for Polysilicon will represent same volume of the Silicon consumed as feedstock into the MCS (Methylchlorosilane - Silicone) production earlier 2000 Is. A closer look into the installed world capacity of Silicon production is also important to give us an overview about the size of the opportunity while the environmental global assessment of the actual assets is considered on this paper: Figures 3 and 4 â World Si/FeSi Installed capacity divided by country/producer source Viridis.iQ GmbH 2|Page Road mapping how

to reduce the environmental emissions and energy consumption for ferrosilicon and Silicon plant In the case of the Ferrosilicon world installed capacity, is important to take a look in the division by producer: Figures 5 and 6 - World Silicon Installed capacity divided by producers (source: Ferroalloys consulting KF) In terms of the division by country, the majority for Chinese producers is also clear. Considering this market overview, allied to the China 13th Five-Year-Plan (2016-2020) discussed and approved in the end of 2015, which cover mainly the Upgrade of Industrial Infrastructure and Green Development as two of the main pillars of the plan, this article will be covering important topics that could be drive the Chinese industrial development towards the 13th Five Year Plan targets. Based on the actual importance of the Chinese Industry into the Silicon and Ferrosilicon world, any movement in direction to reduction of environmental reduction as well as industrial refurbish, upgrade or retrofitting, will strongly impact the market worldwide and the benefits of these movements could be capitalized into the local industries and also globally downstream applications.

2 - Flow Diagram process and Equipment similarities

2.1 - Silicon and Ferrosilicon Process overview:

The metallurgical Silicon process consists basically in the usage of Silica Ore (SiO_2) to be added into the Submerged Arc Furnaces (SAF) together with reducing agents, called reductants such as low ash coal, metallurgical coke, charcoal, char and also woodchips that contributes with the resistivity and porosity of the charge. The mixture of raw material is pre-treated in some cases via washing process, screening and the batching system is very important pursuing the homogeneity of the charge that would be feed on top of the SAF. The smelting process take place into the furnace and needs to be very well controlled into an interface region between the thermometallurgical, chemical, electrical and constructive (mechanical, electrical equipment) areas that permit to achieve the best Silicon recovery ratios and consequently the lower specific raw material, electrode and electricity consumption. That ideal ratios also would consequently permit that the by products such as Silicon Carbide, Slag and Microsilica common for that metallurgical process are produced in its lowest possible ratios, once the highest process efficiency implies in lower by products production.

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Figure 7 - Silicon process overview in basic flow diagram source Viridis.iQ GmbH The figure below gives an overview of the Metallurgical Plant (Si and FeSi): Figure 8 - General plant overview - Silicon and Ferrosilicon source Bateman Engineering

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2.2 - Similarities and main differences:

To present the main differences between the Silicon and Ferrosilicon process, the author shown in the following figures the block diagram of those 2 processes. The SAF considered on the diagram in the next figures are same, around 27MW active power. Figure 8 - Silicon bloc diagram process (source: Viridis.iQ GmbH)

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The mass balance and the reference data base used in the process design above is on purpose hided by the author for IP reasons. The purpose of the image is to present the block diagram and the sequence of the process in a typical Silicon production process. Figure 9 - Ferrosilicon bloc diagram process (source: Viridis.iQ GmbH) The mass balance and the reference data base used in the process design above are on purpose hided by the author for IP reasons. The purpose of the image is to present the block diagram and the sequence of the process in a typical Ferrosilicon production process.

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In general the main differences between the both processes are:

- Global reactions: Silicon: $\text{SiO}_2 + 2\text{C} \rightarrow \text{Si} + 2\text{CO}$ Treaction $\sim 2000^\circ\text{C}$ Ferrosilicon: $\text{SiO}_2 + 2\text{C} \rightarrow \text{Si} + 2\text{CO}$ Treaction $\sim 2000^\circ\text{C}$ and $\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$
- Raw Material - in the Ferrosilicon process, there are required a source of Iron, either Iron Ore (normally hematite/magnetite) and Iron Scrap, for example. In both cases there are different requirements of Silica Ore quality and quantity, the reductant agent and the flux, such as limestone. This will slightly change the process and consequently the off gas generated in the reaction process.
- Electrode Technology - in the Ferrosilicon process, is not recommended, based on the author experience the usage of prebaked electrode, due to economic reasons, which could bring problems from the Operational Expenditures standpoint. The recommended electrode technology is the Soldeberg Electrode with standard steel shirts (case) and steel thins. The electrode is calcining into the contact plates zone in the top of the furnace at temperatures higher than $500\sim 600^\circ\text{C}$. In the case of Silicon, three technologies can be used, including Soldeberg, also called "Alternative electrode technology", composite electrode, and prebaked electrodes. Because the higher aggregate value of the product, as well as the better market conditions, there is room to operate this production process using prebaked electrode, even considering the alternative technologies cheaper ones.
- Refining process - in the case of Silicon refining, the typical higher grades of product should be below 0,020% of Calcium and

sometimes below 0,300% of Aluminium, the required amount of gas injection is normally higher comparing with the Ferrosilicon refining process (for FeSi75 std). In the case of low aluminium Ferrosilicon production process, the required amount of Oxygen and Compressed air (N₂/O₂) is also higher than standard FeSi75 refining. Of course that, for this discussion, the comprehensive mass balance should take place, with the specific consumption, raw material chemical analysis and furnace performance to calculate the accurate amount of gases required for any of those refining processes. e) Electricity consumption due to the higher purity of the Silicon produced (>98,5%) compared with the FeSi considered on this paper (normally >75%); also considering that the Silicon global reaction is endothermic while the FeSi process has more exothermic reactions, the specific energy consumption for the Silicon (10 to 12MWh/t Si) production process is normally higher than for FeSi75 (8 to 9 MWh/t FeSi75). f) Tapping process to produce FeSi75, due to the lower reaction zones and hearth temperature, the discontinuous tapping is the most indicated process to tap the product from the furnace into the refractory ladles. In the case of Silicon, the most common tapping process is the continuous process, avoiding closing the tapping hole during the production process. Some companies in China and a few examples in the Western Silicon producers (less than 5%) use also the discontinuous tapping to produce Silicon, with good recovery Si results as well. This differentiation on the tapping process affects directly the electrical stability of the furnace and consequently the off gas generation as well as the stocking procedures. g) Crushing / Grinding process considering the different application of the Silicon and Ferrosilicon industries, normally the grinding process is not required for Ferrosilicon products. The polysilicon and silicones industries normally require the smaller sizes, in the range of micrometres; this is a different physical process comparing with the standard crushing process, that is normally used to Ferrosilicon and partially for Silicon products (in the millimetres range, typically). This implies in higher losses and dust generation in the case of grinding process of Silicon for chemical industry. Some other differences such as the off gas system design (due to the thermodynamically behaviour on top of the furnace), the casting process, the typical extra addition process of raw material, different characteristics of the slag, different thermal profile of the smelting process and after tapping process and other minor differences between the Ferrosilicon and Silicon production process.

7|Page Road mapping how to reduce the environmental emissions and energy consumption for ferrosilicon and Silicon plant 3 - Environmental Emissions in both metallurgical Processes 3.1 Overview In the introductory topic of the most important chapter of this technical article, the authors will describe briefly the overall process environmental most impactful points and used them as a control volume for the coverage of this technical review. Basically what are the main inputs, processing and outputs of the FeSi and Si general plant are represented in the diagram below: Figure 10 The parameters of the silicon process (Schei, Tuset, & H.Tveit, 1998). Basically what is possible to classify as Environmental Emissions are the following components: Figure 11 Si / FeSi process overview a potential 5R Is (rethink, reduce, reuse, refuse, recycle) source Viridis.iQ GmbH For each part of the process that is any losses, waste or by-product generation, is important to focus in some kind of equipment, procedures or treatment to mitigate the emission, reduce the losses or recycle any potential environmental losses in the process. This article will be qualitatively focused in the environmental emissions reduction as well as the process efficiency increase in order to reduce the specific energy consumption in the Silicon and Ferrosilicon production process.

8|Page Road mapping how to reduce the environmental emissions and energy consumption for ferrosilicon and Silicon plant Besides the importance of implementation, together with the environmental control systems of an effective Environmental Management System, dedicated to be guidance to employees and organization to environmental practice in their activities in order to ensure continuous process improvement. Identifying, preventing and / or reduced the environmental aspects and impacts related to the production chain of Silicon and Ferro Silicon. It is understood as the production chain, the set of activities that progressively articulate from basic raw materials to the final product, including distribution and marketing, being in segments. Considering the whole supply chain process, which should be an extension of the previous concept; starting from the design of the project (environmental feasibility) to its outputs (products and by-products). Thus, elimination and mitigation of pollution should be treated from the time of extraction, handling, preparation and use (power) of the raw material (quartz, wood, limestone, electrodes, wood chips, coal and consumables for example), production and shipping and proper disposal of waste and by-products generated. This article will be qualitatively focused in the environmental emissions reduction as well as the process efficiency increase in order to reduce the specific energy consumption in the Silicon and Ferrosilicon production process. It is suggested then adopt oriented procedures aimed at optimizing the movement of vehicles and mobile equipment, use of biodegradable raw materials and ecologically proven fuels (such as biodiesel), for use in vehicles, equipment

and users machines of this input, and control black smoke through the maintenance of these vehicles, equipment and machinery

3.2 Silicon and Ferrosilicon main emissions: a) Raw Material Handling, Batching and Feeding system:

In the both cases, for Silicon and Ferrosilicon, the difference basically in the raw material used in the process is the source of Iron required for the Ferrosilicon Process. This could be Magnetite or Hematite (more common), the iron ore species (Fe_3O_4 and Fe_2O_3 basically) in some rare cases the Wurstite is also used. Depending on the marketing conditions, the iron scrap is also used in several furnaces around the world. The main problem related to the environmental emissions for that part of the process, actually is the dust generation during the receipt, discharge and screening of reductant (low ash coal, charcoal, char and/or coke), mainly for the producers who works with charcoal which generate a high level of dust during the raw material handling. One of the biggest concern of carbon source handling are related to health and safety because the screening and receive process of reductant needs to be made under enclosure areas, generating an ATEX (Atmosphere Explosive) zones, as shown in the drawing below: Figure 12 - Example of ATEX Classification zone in typical reductant receive station

9 | Page Road mapping how to reduce the environmental emissions and energy consumption for ferrosilicon and Silicon plant Figure 13 - Example of ATEX Classification zone in typical Raw Material Handling System

In both cases, the hachured areas in red, rose and blue, represents the ATEX zones. The definition of the ATEX zones, depends on the characteristics of the chosen raw material, which can substantially vary (e.g. charcoal and coal), and the probability and frequency of dust presence during normal operation. One technical mitigation measure, normally used to reduce the ATEX classified zones in a project is the installation of a simple Dedusting system that collect the fines and dust generated during the raw material receive, screening, weighting and transport at the metallurgical Plant. In the case of Silicon Ore (SiO_2) handling, the screening process is the major dust generator. A common method used in some plants is the washing of the ore during the screening process, before feeding to the furnace. The utilization of a washing system eliminates the need of utilization of a dedusting system during the SiO_2 screening. In this case the fines will be dried and disposed according to the regulations and the water will be reused. For plants that do not use the washing system, the environmental emission elimination can be done via a simple de dusting collection system containing hoppers, id fans and a bag house to collect that dust. According to the installation design, the utilization of one of two dedusting systems for the raw materials will be defined. Modern plants design normally considers the installation of one dedusting system for the receipt and discharge system and one for the raw material handling, batching and furnace feeding system. Normally, the silicon ore dust could be used in the concrete and/or another metallurgical silicon application, such as silicon manganese hot area or refractory preparation. In the case of liquid effluent generate during the washing process, the neutralization of the material could be required in a simple water treatment station via chemical treatment, depending on the characteristics of the effluent as well as the local environmental regulations. In any case, the Environmental Impact Assessment (EIA) must to consider any possible environmental aspect caused in both cases. In the case of limestone, there are no environmental emissions that required further treatment. Normally this flux is dosed in minimum quantities in the feeding and batching process, as well as in the top of the furnace via stocking machines or manually. In the case of the woodchips, for the plants which receive the wood logs and process that raw material at the plant, in woodchopper machines, which will cut and screen the woodchips produced, the amount of generated dust do not requires the installation of a dedusting system, but the fines needs generated needs to be correctly disposed, one of the possible uses is as biomass for ladles preheating. In the figures below is possible to see an example of raw material handling system dedusting equipment, in different parts of the world. For the base case scenario, the expected level of investment could oscillate between USD 2 and 4 Mio (Raw Material Receipt, Handling, Feeding and Batching dedusting systems). Substituir figura abaixo (Reverse Air Cleaning) 10 | Page Figure 14 - Schematic view of the simple dust collection system

Road mapping how to reduce the environmental emissions and energy consumption for ferrosilicon and Silicon plant The following pictures show the example of real dedusting system, with and without cyclone. Normally in Silicon and Ferrosilicon raw material handling systems, it is necessary the installation of cyclones to avoid premature damage of the filter bags by the impact of the dust particles, especially the SiO_2 particles. That is the same reason for the utilization of the cyclones on the crushing and grinding dedusting system, which will be discussed further on this technical article. Figures 15, 16 and 17 - Typical dedusting system for Raw Material Handling System (w/wo cyclone) Images (a) and (b) show the outside raw material dedusting systems which the (c) shows the enclosure raw material batching and feeding system inside the furnace buildings. In terms of environmental emissions, the fact that Ferrosilicon plant uses the different type of ore as iron source, do not impact the

overall emissions for the plant, comparing with the Silicon raw material handling system. During the batching and feeding system, the weighing and mixing of the different raw material could also generate some dust. These environmental emissions are not poisons but the carbon dust presence in the air could lead to an increase in the ATEX classified zones extension, be harmful in terms of comfort for the operators, and also the cleanness of the furnace building area. For this reason, a regular dedusting system (bag filter, pre separator, fans, stack) needs no be considered including the installation of dust collection suction points for all belt conveyors, weighting stations and transfer points, until the feed of the typical furnace bins that will receive the homogeneous mixture before to be added into the Submerged Arc Furnace. Considering as base case scenario, a plant with 3 submerged arc furnaces of 40,5MVA as apparent power (around 27MW active power), the volume to be handled of raw material and the expected dust generation would be in the same order of dimension for metallurgical silicon or ferrosilicon production, which will represent very similar dedusting systems for the raw material handling system. A complete raw material handling system including the correspondent dedusting system is hypothetically represented in the figure 18 in the next page. Figure 18 â Base case scenario 3D plant overview â hybrid plant source: Viridis.iQ GmbH (in detail the bottom TENOVA) It important to consider the usage, based on specific project characteristic, devices for wetting system and cells of raw materials and products as suppressor use of polymer powder. As for transportation, use of closed or covered by tarpaulins vehicles, conveyors or covered mats. In the case of handling products and raw materials in warehouses using industrial exhaust fans that mitigate the particulate material dispersion (in specific cases, the material can be reused) which would be discussed in detail in this article. 11 | Page Road mapping how to reduce the environmental emissions and energy consumption for ferrosilicon and Silicon plant b) Stocking Process, Off gas system and heat recovery in SAF Normally, in the Ferrosilicon and Silicon production process, the submerged arc furnaces used are semi- closed or semi-open in the burden of the raw material, in the top of the furnace, as presented in the following pictures in the next page. Figures 19 and 20 â Picture of FeSi furnaces â Semi-closed (source SMS)/Semi-open (source VAIBHAV) Figures 21 and 22 â Reference picture of Silicon Furnaces â Semi-closed (Elkem) / Semi-open (Elkem) The fact that the submerged arc furnace, either for Ferrosilicon or Silicon has a semi-closed or semi-open characteristics, would impact significantly in the off gas system used to collect the gases from the reaction inside the furnace. Based on that, under this sub-topic, we are going to briefly explain the Viridis.iQ off gas model based on thermodynamics, heat transfer and fluid dynamics in the top of the furnace. The off gas model: For simplicity purposes, the off gas model would be presented and could be applicable either in Ferrosilicon of Silicon production process. The thermodynamics are slightly different between the two mentioned process because the raw material and the reaction kinetics are different, which bring to different thermo-profile in the top of the furnace. Normally, at the same ideal construction conditions (well-designed submerged arc furnace with the good diameter/height/electrode dimensioning/electrical input) and the similar good operational conditions, similar good raw material characteristics; the top of the Silicon submerged arc furnaces have higher temperatures in the top of the burden compared with the Ferrosilicon submerged arc furnaces. Basically, this different is due to the reactions characteristics (exothermic / endothermic). Figure 23 â Top of the submerged arc furnace â Viridis Model Basically, the heat transfer equations used into this off gas model are: Thermal resistance for conduction, convection and radiation. 12 | Page Road mapping how to reduce the environmental emissions and energy consumption for ferrosilicon and Silicon plant What happened in the top of the furnace basically is the off gases come from the hearth reaction zone, at high temperatures and there is outside air that wills entry in the top of the furnace from outside. That outside air basically is partially use as combustion air to exothermically react with the CO that come from the reaction zone (both cases, Ferrosilicon and Silicon process) and part of that outside air will also be called the cooling air, which basically will exchange energy under heat form with the gases coming from the reaction zone and the kinetics dynamically happening in the furnace. During the process, basically what come out from the furnace, in a stable operation reference, are CH₄(g), N₂, H₂ end others volatiles (like C₂H₂), H₂O(g), CO(g) and SiO(g) from the reaction process. Besides the fact that is very difficult to predict the temperature of those gases, some measurements have been done and to use as calculus basis, the author considered the typical off gas temperatures in the range of 450oC to 600oC coming out of the furnaces (normally, 20 to 25%) higher for Silicon process compared with FeSi in the very same conditions as mentioned above). Those gases initially entry in contact with the outside air that at once partially exchange energy (cooling air) and chemically react with part of those off gas reaction zone gases (combustion air). There are strongly and simultaneous reactions and thermal gradients oscillation at once in the top of the furnace. For dyadic purposes, the authors would assume, based on the off

gas model that the temperature raise immediately to, around 1000°C, in the combustion cloud and afterwards drops to, let's say 500°C to 600°C immediately after to entry into the furnace chimney, to the off gas system equipment. The thermodynamic overview of the reactions in the top of the furnace could be verified in the figure below, the schematic thermodynamic simulation model for the submerged arc furnace off gas design. Figure 24 - Thermodynamics and kinetics in the top of the submerged arc furnaces. What are going to change basically between the FeSi and Si process model are the volatiles and the thermal behaviour in the top of the furnace. Considering that the main purpose of this article is to explore qualitatively (mainly) the environmental emissions reduction, the quantitative analysis of the volume of the gases would not be deeply analysed on this article, but the typical off gas equipment and some behaviour of the off gases during the stocking and as reference some suggestions to minimize those environmental emissions. The batching & feeding plus the stocking process have directly impact on the gases volume and the behaviour in the top of the burden of the submerged arc furnace, either in Silicon and Ferrosilicon.

13 | Page Road mapping how to reduce the environmental emissions and energy consumption for ferrosilicon and Silicon plant production. Recently some measurements done at Elkem Thamsarvn confirm the directly relationship between the environmental emissions and these process, as presented in the next figures. Figure 25: NO and the coherence with Silica fume (Kamfjord). The frequency, operational procedure, batch design, mass balance and characteristics of the equipment and machinery impact directly in the off gas generation and the process environmental emissions. During the combustion process in the top of the furnace (off gas from the reactions with the combustion air from outside), NO_x can be formed by thermal, fuel and prompt mechanisms (De Neves, 2000). The hydrocarbons in the volatiles that come from the reducing agents (mainly) have important influence there. The outside air brings a lot of Nitrogen and Oxygen, this also contributes tremendously for the NO_x formation in the Silicon and Ferrosilicon submerged arc furnaces, at higher temperatures. Zeldovich mechanism reaction: $O + N_2 = N + NO$ $N + O_2 = O + NO$ And extended Zeldovich mechanism reaction: $N + OH = NO + H$ And, $O_2 = 2O$ Based on the free Gibbs energy equations and the mechanism, the formation equation is the following for NO_x: (Integrating) Figure 26 - The Zeldovich mechanism representing the formation dependency of temperature. As a primary requirement for any type of Submerged Arc Furnace to be used into the FeSi and Silicon production, the off gas system is mandatory. From the environmental standpoint, considering the base case scenario (3 x 27MW SAF), in the case of all 03 SAF producing Silicon, the gases volume generate on those 3 furnaces in yearly basis would expected to be up to:

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Component (wastes)	Yearly generation (max)
Micro silica	20,000 t/year
CO ₂	340.000 tons/year
NO _x	1,256 tons/year
SO ₂	1,675 tons/year
PAH	78.50 kg/year
BaP	2.10 kg/year
POP	1.05 x 10 ⁻⁶ kg/year

Figure 27 - Estimates table waste for Base case scenario operating with 100% of low ash coal, producing Silicon. The off gas system would be responsible to capture all the wastes generated in the top of the furnace and these wastes could be capitalized and for this base case scenario, the microsilica that can be captured and sold as by product. Considering the average price of USD200/mt of Microsilica (at lower quality level), the potential revenue for this base case scenario is equal to, 20.000mt/year x USD 200/mt = USD 4Mio/year of revenue. Of course the a comprehensive financial analysis should be done for that type of project, but if you very basically consider that such off gas system will requires around USD 20 to 25Mio, and considering the operational and maintenance costs listed on the table below, and based on that briefly calculation, it's possible to consider around 9 to 10 years return on investment (RoI). The batching, feeding and stocking process are fundamental for the Silicon and Ferrosilicon processes. The main impacts generated for those processes are:

- Charge homogeneity
- Gas generation (NO_x formation)
- Process Stability and Efficiency (energy consumption)
- Off gas temperature
- Micro silica quality control

Depending on the electricity local prices, the equipment design and the company owners' appetite for investment on environmental and excellence initiatives, the Heat recovery also is an important topic related to the off gas design that could be considered for Silicon and Ferrosilicon submerged arc furnaces.

Annual Energy Costs	Number of ID Fans (One per furnace)
900,00	3 ID Fan
900,00	Power (KW)
24	Operation Time (h) Days per year
365	Price per KWh (US\$)
0,03	Total Expected Annual Energy Costs
709.560,00	Total Expected Maintenance Annual Costs
MioUS\$	Maintenance and Other Annual Cos
1.250.000,00	Bag House Hair Pin Cooler Microsilica bin Cyclones

Figure 28: Illustration of a typical hot gas cleaning system (source Viridis.IQ GmbH). Initially, we can see in the figure above, a typical off gas cleaning system. If the off gas do not consider the heat recovery system, the process that are fundamentally considered on that kind of system consists on a duct responsible to transfer the gases from the furnace stacks to the dedusting system and at this duct normally is installed the off gas measurements

systems, which can be a venture, a heat exchange system, normally an 15 | Page Road mapping how to reduce the environmental emissions and energy consumption for ferrosilicon and Silicon plant hair pin cooler for example, that will lower the temperature off the gases from the furnace to the baghouse operational temperature, one equipment to act as separator of sparks and particulates (could be a spark arrester simply and/or different types of cyclones), the bag house where the microsilica is collected and the silica fume densifying system, where the silica is densified, stored and packaged. The Typical dimension for the system may vary between 8.500 to 13.500Nm³/h.MW, depending on the process, the product, and the technology, raw material and design. For the case of heat recovery systems in the off gas equipment of submerged and electric arc furnaces, one of the common systems is demonstrated in the Tenova schema below: Figure 29 â Recovery waste system for Electrical Arc Furnaces (source: Tenova) As reference, the author shows below, a Grassmann diagram of the furnace 3 at Elkem Iceland Grundartang, based on the calculated results from the model published by Hjartarson, et.all during the 20th Ferroalloys conference in 2010, in Helsinki, Finland. Figure 30 â Grassmann diagram FeSi furnace 3 â Elkem Iceland (ratios of the streams are based on the input). Based on the energy balance presented above, is possible to confirm the international results that companies like SMS Siemag, Tenova Pyromet, Resonant and others are claiming in terms of Heat Recovery for Silicon, Ferrosilicon and other Ferroalloys submerged arc furnaces, the range of 20% to 40% of energy recovery in the heat recovery systems, depending on the furnace technology. Considering a range (in case of Ferrosilicon furnaces) of 8,5MWh/t of FeSi, using the base case of 3 x 27MW furnaces (now producing 80.000mt/y of FeSi75 std), will means a yearly consumption of 680.000MWh/t. Considering the electricity price of USD30/MWh (competitive prices within the Silicon industry, for example â Viririds estimates) and the potential energy recovery of 25%, this will means a potential electricity consumption reduction of 20% x 680.000MWh/y = 136.000MWh/y. In terms of economy, the estimated value would be more than USD 3Mio per year (136,000MWh/y x 30USD/MWh â operational and maintenance costs). Considering the total investment for this system around USD20Mio, this will mean a return of investment around 7 years (if you add the NPV calculation here). The design of the equipment (stocking machines, batching and feeding system and the furnace itself) are very important and would impact positively the efficiency of the process. In some cases, the overall equipment efficiency can oscillate in the range of 10% to 15%, directly impacting the energy consumption of the furnace; depending on the procedures, process control and management of the production process. In terms of Silicon production process, this could mean a specific energy consumption reduction, for example, from 13MWh/t of Silicon to 11MWh/t, circa 2MWh/t of Silicon. 1 16 | Page Road mapping how to reduce the environmental emissions and energy consumption for ferrosilicon and Silicon plant Considering the base case scenario of 3 x 27MW furnaces producing Silicon, this will mean around 55.000mt/year which implies on 110.000MWh/year just in the Specific Energy consumption reduction. Considering the benchmarking of electricity price nowadays around USD30/MWh (competitive electricity prices for Silicon/FeSi plants, for example, based in Viridid estimates), this process improvement will represent more than USD3Mio per year in process optimized results and soft money into the cash flow of the plant. Of course such a kind of result normally not depend on exclusively one process of the entire plant, but a conjunct of action that will drive the operational excellence of the plant towards world class results level company. Anyway, the environmental opportunities in any part of the Silicon and/or Ferrosilicon process almost all the time would represent benefits in terms of cash flow, soft or hard money and it worth most of the times invest on that kind of initiatives. Figure 31 â Example for the off gas system in Ferrosilicon plant in China (Erdos) Figure 32 â 3D design of 4 x SAF heat recovery and off gas Ferro Alloy Plant (source Metix) c) Tapping Process (continuous and discontinuous process) Another very important environmental emissions point for the Ferrosilicon and Silicon production processes is the tapping. This process is exactly the part of the production process where the liquid Silicon or Ferrosilicon is tapped from the SAF into the refractory ladles. This step is very important in terms of efficiency and quality of the operations of the metallurgical plant. During the tapping, the furnace operators are responsible to keep the channel clean enough to permit that the liquid product come out of the furnace in temperatures that could easily reach the 1650oC. During all the tapping process, there are fumes and gases coming from the reaction zone, inside the furnace. Those gases volumes are considerably high and during some process unbalancing typical situations, the SiO gases coming from the furnace could increase tremendously. The process gas in most reduction furnaces to produce Silicon and Ferrosilicon product is mainly CO as shown in general equations initially presented here. The SAF interior present normally, the slight positive pressure due the conversion of solid materials (iron ore, silicon ore, reducing agents, flux, etc) into the liquid and gas phases; which occupies higher volume compared with the solid raw materials input

into the SAF. 17 | Page Road mapping how to reduce the environmental emissions and energy consumption for ferrosilicon and Silicon plant Based on previous studies reference of H.Tveit et.all, in large industrial (Ferro) silicon operation, 1 litre of solid materials is converted to around 3000-5000 litres of gas, this creates up to 0,07bar of positive pressure inside the Submerged Arc Furnace. The operational tap hole condition must be kept as controlled as possible. There are in the Silicon and Ferrosilicon industry process oscillations, operational instability control and not ideal operational conditions could cause problem during the tapping process, bringing problems to keep the channel free of slag and products that could clogging the tapping hole. In this case, the positive pressure inside the reaction zone previously mentioned, plus the liquid material that is accumulated inside the furnace, can, for example to favourably dislocate the equilibrium and thermodynamics towards the back reactions, which will generate the SiO and CO gases that, will anyway find a path to get out from the furnace (even considering the obstruction of the tapping hole). Those gases will react immediately with the outside air (due to the lower thermodynamic stability at lower temperatures) which are exothermic reaction and will surely create heat that could be harmful and increase the gas volume via the SiO₂ amorphous generation and CO₂ as well. Those particles are environmental emissions that can pollute the plant environmental and give rise to diffusive emissions. Based on the same study mentioned previously, those particles normally are smaller than 2.5 µm, making them respirable, and a fraction of these particles is also under 100 nm (Kero, Næss, and Tranell, 2013). A computational fluid dynamics (CFD) simulation of velocity distribution of tap-hole exit gas on a scale from 0-65 m/s in the tapping region is shown in Figure 2. The jet will leave the tap-hole with a velocity of approximately 50 m/s and may become more than 3 metres long (Ravary and Laclau, 1999). Figure 33 - Gas velocity distribution for the tapping off gas (Ravary and Laclau, 1999). Based on that conditions, is fundamental to have an efficient off gas collection in the tapping hole of the Ferrosilicon and Silicon furnaces. Those types of reactions happening inside FeSi and Silicon submerged arc zones generate inside the furnace hearth, into the reaction zones, pressure increase, mainly in the crater zone. That high pressure is due to the reaction gases generated inside the furnace and those gases flows towards furnace top through passing the charge materials, as well as towards back to the tapping hole of the furnace, normally the tapping hole that has been used in the production process. That SiO condensation (the major contributed to this pressure increase), can be show as the following reaction: $SiO(g) = Si(l) + SiO_2(s,l)$. The distribution of those gases flows will be directly affected by the charge homogeneity of the charge, the permeability, as well as the porosity of the mixture inside the SAF. The pressure phenomena inside the submerged arc furnace for Silicon and Ferrosilicon process depends, besides the mentioned parameters above, the humidity of the charge, the operational regime that the furnace has been operated and the control of the electrode length, as well as the electrical parameters inside the furnace, in the figure 34, is possible to see a schematic of SAF inside. 18 | Page Road mapping how to reduce the environmental emissions and energy consumption for ferrosilicon and Silicon plant Figure 34: Schematic of furnace inside and the tap hole gassing phenomena [22] In the technical article from M. Kadkhodabeigi [21] it was presented some measurements of the pressure into the Elkem Thamshavn FeSi furnace. Figure 35 - Measured crater pressure and electrode load at Elkem Thamshavn [1]. The pressure oscillates over the time and also has a direct relation to the furnace Load. It is well known that that gases velocity (m/s) and the furnace active power (MW) obey a quadratic relation as follows: $gas\ velocity\ [m/s] \propto Active\ Power^2\ [MW]^2$. This could explain the big oscillations comparing different SAF sizes. The tap hole process gases will immediately, as soon as it comes out from the furnace via tap hole, reacts with the outside oxygen from the atmospheric air and the main products generated will be SiO₂(g) and CO₂(g). Those are exothermic reactions and the temperature of the surround sharply increases when the gas volume increase. This is a significant internal pollution source and must be collected somehow, via secondary dedusting systems in the Silicon and Ferrosilicon plants. Previous numerical models based on empirical research shows that the gas velocity of Silicon and Ferrosilicon furnaces could oscillate from 10 to 100m/s. For that range of gas velocity, the gas volume in the tapping process could reach up to 60.000Nm³/h, based on the Elkem FeSi furnaces in Norway (study reference). Figure 36 - Evolution of maximum flame temperature vs gas velocity (measured in FeSi75 furnace in Elkem) The graph of figure 36 shows that, the tapping gases temperature increase tremendously with the gas velocity, stabilizing around 35 to 40m/s and temperatures in 4.800 K. Although the main gassing outlet either in Silicon and Ferrosilicon processes happens in the top of the furnace, the tap hole process gassing presents a considerable volume, which represents safety and health risk for the operations, and also environmental emissions risks. Some exemplary images are presented in the following figures: 19 | Page Road mapping how to reduce the environmental emissions and energy consumption for ferrosilicon and Silicon plant Figures 37, 38 and 39

â Tapping hole gas collect hood â Elkem Thamshavn For this specific base case scenario (used in this article â 3 x 27MW), the author recommends a detailed engineering study but the expected range for such system, considering the 5 tap holes per furnace, the capacity for the tapping hole collection dust should be in the range of 45.000 to 60.000Nm³/h per furnace. A typical solution on newer plants design is the utilization of the gases collected from the tap hole through the ID fans, hoods and ducts, to insufflate air in the feeding ducts under the furnace bins and to insufflate air in the electrode sealing. The main benefit of this solution is that it eliminates the need of additional insufflation system, therefore reducing the investment and operational energy consumption. Another possible solution is to connect these ducts to the main furnace stacks. In the case of the existing old furnaces, itâs not possible to implement these solutions without big changes. The most common solution in this case is the installation of a separate dedusting system. The Micro silica collected in this treatment system bag houses will be slightly better in terms of the quality, compared with the microsilica generated in the main off gas system. Normaly this system is connected back to the furnace. The author suggests a comprehensive feasibility study for brownfield installations, the implementation decision needs also to take in consideration the actual environmental regulations, in many countries requires the installation of this type of equipment. For Greenfield projects or furnaces, the installation of the collection tapping hood is a mandatory component of the installation. This investment will be very specific for each part of the world, but per furnace, the total investment would not expect to exceed USD 3 to 4 Mio, in total for the 3 SAF.

d) Post treatment process â Refining, Casting, Material handling Process The first and very simple step to reduce environmental emission during the liquid Silicon and/or Ferrosilicon at high temperatures is to implement the product handling procedure with installation of cover on top of the refractory ladles. This measure could help also to reduce the material losses adhered in the internal walls of the refractory ladles, impacting instantaneously in the process output. This initiative would also impact positively in the standard gas refining process, reducing the thermal losses by radiation or convection during the refining process. Figures 40, 41 and 42 â s 3D overview of the casting station (Tenova), the US Patent for top ladle covers number US 5065987A. There are several types of Refractory ladles top covers, designed specifically for each singular application process and equipment (ladle) design. Normally, the top cover should be protected by the refractory (high Alumina, for example), due to the high temperatures which that covers are normally exposed (>1000oC, in some cases). For the base case scenario, the total investment is expected to be in the range of USD 0.5Mio to USD 1Mio for the ladle top covers installation. The post treatment process mentioned here representing lower environmental emissions compared with the previous discussed process. The casting process used in the Silicon and Ferrosilicon Industry has different technological routes, as mentioned below:

a) Standard casting process â on this case, the liquid Silicon or Ferrosilicon is casted in solid moulds made by Iron (casted Fe) or Silicon and covered by Silicon fines (in case of Si casting) and this process consists in cast the liquid product in independent moulds, in separate and discontinuous processes steps. The operational risk for slag contamination during this casting method is normally higher than the others casting methods that will briefly be mentioned on this article. In this case, dedusting equipment are normally bigger, when compared with continuous casting process, which use one to four suction points above the casting tables, dumpers are installed in the suction points to allow the selection of the respective hood. This type of dedusting, for the base case scenario is 20 | P a g e Road mapping how to reduce the environmental emissions and energy consumption for ferrosilicon and Silicon plant expected to be in the range of USD 2Mio to USD 3Mio for all the plant, including the equipment of the system. In some cases, in order to reduce that costs, some technology companies are installing the suspended rails where the smaller hood can move during the casting, being on top of each mould during that specific casting time. The expected flow in this area for the base case scenario is around 160.000 Nm³/h Figure 43 and 44 â Casting picture and dedusting system example (Tenova) b) Continuous casting â the authors have very good experience with this type of casting, slag free and lower costs applied for gases dedusting. The difference basically is that the moulds, normally made by Casted Iron and/or Silicon and covered by Silicon fines are connected and the entire conjunct has a smooth slop from 3o to 6o, depending on the design. The casting point is a singular point in a type of âboxâ where the liquid Silicon or Ferrosilicon are casted, between that âseparation boxâ and the moulds interconnected conjunct, there is a single step degree where the liquid product runs. Figure 45 and 46 â slag free continuous casting process (source Viridis.iQ GmbH) For this type of casting, the single suction point is enough and the complexity of the off gas hood for the casting process is considerable cheaper. One design solution in this case considers the connection of the suction duct to directly to the furnace stack together with the tapping hood duct, another solution is to use the gases to establish a insufflation system for the furnace

bins together with the ducts from the tapping hood, and a third solution is to install a secondary dedusting system for the casting area. Figure 47 - Example of de dusting system for casting process (source Tenova)

There are also different types of Casting well know and used in the Silicon and Ferrosilicon Industry, like carrousel (Ferroatlantica), and copper water cooled casting table (developed by GFAT and similar casting design copper cooled table used in producers of Silicon, in Germany, for example). 21 | Page Road mapping how to reduce the environmental emissions and energy consumption for ferrosilicon and Silicon plant

Figure 48 - schematic view of the casting table developed in the Ferroatlantica Group Figures 49 and 50 - Carrousel casting table developed in FeSi and Silicon production and example of fumes during casting. For casting process, the financial return on investment is a more complicated argument to build in a potential business case. By the way, in terms of environmental emissions regulation, every day the law is becoming more restrictive and the charges by the environmental regulatory agencies is getting more and more expensive. Some Silicon producers in Brazil had to sign official conduct term of adjustment to keep some of their factories in operation, due to the high environmental emissions and pollution caused by those plants, in Minas Gerais mainly. There are other two processes that also can contribute to the internal plant pollution increase, the preheating and refractory cleaning process of the ladles and the Refining process. For the preheating processes, normally some companies had developed the Biomass usage to preheat the refractory ladles immediately before to send those equipment for the tapping process position start. More common the usage of LPG (Liquefied Petroleum Gas), but some companies had developed its own method to burn its own process biomass (barks, leaves, fines of woodchips, etc) during the preheating process. For this process, the environmental emission solution is to install in the furnace area, preheating covered suction stations that capture the combustion gases from the preheating process and could be used in internal energy recovery to heat up water or another internal usage. The system is not complex and not so expensive, due to its simplicity. For the refining process, there are also coming from the gases some chemical oxides such SiO (g) that reacts with Oxygen in the Air and generate SiO₂ (s), Al₂O₃ (g), CaO (g) and other minors oxides such as TiO (g). The typical refining process used in Silicon and Ferrosilicon process is the slagging oxidative process, where dry clean compressed air is injected via plugs in the bottom of the refractory ladle, normally mix with pure oxygen. The oxidation reactions generate a considerable amount of gases (normally is used up to 20Nm³/h per ton of Silicon refined), as presented in the schematic following figure: Figure 51 - Schematic refractory ladle with plug and the overview of the reaction in the oxidative refining (source Viridis.iQ GmbH) In order to reduce the environmental emissions during the refining process is important to keep the top cover for the refractory ladle during all the process (gas injection) as well as to define the fixed position for refine of the Silicon or Ferrosilicon. The gases collected during the refining process are hot and there are some potential to re-use those high temperature gases in internal application or heating process for administrative or laboratory usages. 22 | Page Road mapping how to reduce the environmental emissions and energy consumption for ferrosilicon and Silicon plant e) Milling, Crushing, Grinding, Screening and Packaging Process For milling units, the crushing and screening process, there are some recommendations to enclose the systems and install some pollution control systems in order to minimize that pollution generation. The solution normally used is the installation of a regular pulse jet dedusting system coupled with a cyclone. The installation of this type of equipment is required even for the crushing in the range of millimetres, due to the fine dust -micrometres- that is generated during the crushing and screening activities. Some examples could be presented in the images below: Figure 52 - Crushing and screening system examples (Silicon and Ferrosilicon usage open source) In the case of Grinding Silicon mostly, in the range of -micrometres-, the safety and healthy risks are considerably big and is mandatory to intall a protection system. The solution normally used is also the installation of a regular pulse jet dedusting system coupled with a cyclone. Deping on the complexity of the design some technical solutions includes the neutralization of the entire systemwith Nitrogen, for example. Some example of pictures can be seen in the following schematic drawings and figures: In both cases, crushing and grinding systems requires a ATEX classification study that will evaluate the protective measures adopted according to the design solution and define the electrical equipments that should be used for each system. It is mandatory the instalation of explosion vent panels, rupture plates on the pulse jet bag houses. Figure 53 and 54 - Schematic 3D grinding system fo r Silicon (source Viridis.iQ GmbH) Is also important to mention that there are in the market, different types the crushing and different project types. The correct system dimensioning, based on the input and output in terms of size is one of the most important factors to achieve a good design. Once the design is correctly dimensioned, the energy consumption is low, the risk for quality, safety and health also is lower and the environmental emissions are also lower. Generally, the prebreackage station with a grizzly feeder or

(pre) jaw crusher is installed to make the first impact of the casted solidified Silicon before the crushing unit. This also would mean lower fines generation and lower reprocessing of the material, either Silicon or Ferrosilicon. In some plants, there are different post treatment of Silicon and Ferrosilicon and, in that cases, the environmental emission aspect should also be respected and deeply investigate in order to avoid pollution internally of the plant and in the neighbourhood. 23 | Page Road mapping how to reduce the environmental emissions and energy consumption for ferrosilicon and Silicon plant For example, there are some producers of Ferrosilicon that use water granulation to produce granulated Ferrosilicon. In the past, some Silicon producers also follow the water granulation routes Figure 55 and 56 – water granulation processes of (55) Silicon and (56) Ferrosilicon (source google and UHT) In case of Ferrosilicon, UHT had developed recently the Granshot water granulation technology with good operational results: Figures 57 and 58 – granshot plant at Voestalpine, Donawitz and schematic drawing of Granshot System (UHT) in Sweden. In specific case of Silicon, the atomization of liquid Silicon, as well as the recycling of the fines generated in crushing (up to 2%) and grinding (up to 3%), will reduce the overall production costs as well as to minimize the environmental emissions due to the recycling factor and based on the fact that the atomization process happens in a closed chamber, with inert gas such as Argonium or Nitrogen and the temperature and the environmental is total under control, avoiding the pollution source such as in the Electrical Arc or Induction furnaces, used in some cases to reduce these process losses and underflow material coming from crushing, screening and grinding processes. Figure 59 – typical atomization unit design (source: Viridis.iQ GmbH) Some of those post treatments beside the fact that could reduce the environmental emissions significantly, also can generate –premium– classes of products for specific downstream applications like chemical sector, for example (Polysilicon TCS, Silicones MCS). There are some further refining process applied to metallurgical Silicon, for example, that can generate Solar Grade Silicon, but this part of the PV Supply Chain would not be covered in the present technical article. 24 | Page Road mapping how to reduce the environmental emissions and energy consumption for ferrosilicon and Silicon plant 4 – Overall process efficiency and benchmarking 4.1 – Silicon and Ferrosilicon Benchmarking Energy consumption and Silicon Recovery Silicon (Si) is the second member in the Group IVA in the periodic system of elements and does not occur free in nature, but only in combination with oxygen. Most of the Earth's crust is made up of silica (quartzite, silicon dioxide, SiO₂) and miscellaneous silicates comprised of silicon, aluminium, magnesium, oxygen, and other elements. Silicon constitutes about 27% of the Earth's crust and is the second most abundant element by mass, after oxygen. Silicon is not a metal by strict definition because it does not conduct electricity. It is often called a metal due to its lustrous, metallic appearance, but metalloid or semiconductor is the correct designation. Ferrosilicon (FeSi) is a shiny, gray metalloid that is used as a key raw material in many important industrial processes. It is typically an alloy comprised of about 75% silicon and 25% iron, however, the composition can vary depending on the end-user's requirements. The production processes for metallurgical-grade silicon (mgSi) and ferrosilicon and are very similar in principle and involve the reduction of silica – chemical change to remove the oxygen from SiO₂ – with a carbon source in a SAF. The major difference between the production processes is that iron, in the form of iron ore or scrap steel, is also added to the furnace charge mixture for ferrosilicon production²⁴. The ideal conditions toward an world class operational excellence level could be achieved in the interface of the ideal raw material conditions (chemical composition, physical characteristics, moisture levels, fines, homogeneity of the charge, permeability and porosity, etc), the good construction design of the submerged arc furnace as well as the core components such as electrode column, transformers, raw material handling system, top roof of the furnace, off gas, etc) that robust operational control and plant troubleshoot plan, the metallurgical and thermodynamic balance of the process. All those topics would permit that the operational conditions of that furnace and consequently the plant are enabling the operational staff to achieve benchmarking levels of Silicon Recovery and Thermal Efficiency of those equipment. This will reflect into the key process indicators such as energy consumption, electrode consumption, raw material (specific quartz consumption, reducing agent consumption, woodchips, etc) and the output of the plan consequently. The Viridis.IQ had developed the Operational Excellence Diagnostics for Silicon and Ferrosilicon production process that basically take a –picture– of the process and the opportunities on that very specific plant, from the equipment, technology, process, procedure, environmental, health, safety and quality risk assessment standpoint. On that Diagnostic, there is also a classification of the quick hits (low hanging fruits) that could be immediately implemented without any considerable investment and also the short, medium and long term opportunities that must match the business and strategic company plan. Partial Results after 6 months: 1 SAF – Silicon production: Electricity consumption 15,1% reduction (+2,1Mio/s) Electrode consumption: 36,4%

(+0,6Mio/s) Quartz consumption 2,86 to 2,65kg/ton Increase 2202 quality level production in the plant. Significant elimination of the electrode breakage on the pilot furnace used for the operational excellence project. Environmental emissions reductions significantly. Microsilica quality increase. Figure 60 â example of operational excellence diagnostics In any case, the return on investment related to the already applied Diagnostics and operational excellence plan by Viridis.iQ GmbH (based on Lean Six Sigma and PMI best practices) exceeds the USD3,2 per dollar invested in the initial 6 months of application. 25 | P a g e Road mapping how to reduce the environmental emissions and energy consumption for ferrosilicon and Silicon plant 5 â Summary of the main Opportunities 5.1 â China Is 13th Five-Year Plan (2016-2020) (simp.Chinese: ä, -å½ä'èjâ; trad.Chinese: ä, -ää'è) According to the plan the focus will be on the transformation of the economy by means of structural reforms and upgrading of the industrial sector by generating more technological progress, improvement in environmental protection as well as the overall increasing prosperity of Chinaâs population. The 5-13 China SP is a blueprint that details the governmentâs main policy goals and development initiatives for a period of five years. The event of the 18th Communist Party of China (CCP) Central Committee, which took place during 26-29 Oct 2015, approved the CCPâs 'Opinions' on the 13-5 Plan, which covers the period from 2016-2020. Based on the CCPâs Opinions, the government will then formulate an âOutlineâ of the 13-5 Plan, which was approved at the annual National Peopleâs Congress meeting in March 2016. Part of the topics is in line with the main topic of the present article. The pillars and sub-topics are described below. 1) InnovativeDevelopmentasthebackboneofthenewdevelopmentparadigm a. Develop new drivers of development b. Establish new spaces for development c. Upgrade industrial structure d. Strengthen innovation in 4 science and technology e. Modernize agriculture f. Deepen institutional reforms 2) Coordinated Development a. Coordination among regions b. Balance between rural and urban areas 3) GreenDevelopment a. Accelerate the Development of Functional Regions b. Conserve Resources c. Environmental Protection d. Harmonized Development Between Nature and Mankind 4) OpeningUp a. The âtwo-way opening upâ and 1 trade structure upgrading b. Actively participate in global economic governance c. The Belt and Road Initiative d. Reform institutions for international integration The sub-topics covered by the âGreen Developmentâ pillar, allied to the innovation are the topics more related to this technical article. 5.2 â Capitalizing the opportunities. Based on market data of 2013 and 2014 (CRU, Viridis Estimates 2013, 2014), the average of specific electricity consumption of the Chinese Silicon furnaces with the Western Silicon furnaces have a delta in the range of 10% to 14% (up to 1,3MWh/t). Some western producersâ benchmarks are achieving around 10,4MWh/t of Silicon. Considering that, the operational excellence implementation in part of the Chinese furnace, with the potential of reduce the gap by half, from 14% to 7% of difference, this will mean per ton produced, around 600 to 650KWh. The China Is 13th Five-Year Plan, are a series of social and economic development initiatives. This planning is a key characteristic of socialist economies, and one plan established for the entire country normally contains detailed economic development guidelines for all its regions. In general terms, the Chinese initiative is fundamental to the local industry development in the upcoming years. Adopting the 13th five year plan, China has introduced the political, economic and social guidelines for the coming five years. 26 | P a g e Road mapping how to reduce the environmental emissions and energy consumption for ferrosilicon and Silicon plant The actual electricity price in average is around 59,5USD/MWh in China and 30USD/MWh for competitive electricity prices (Viridis Estimates 2016), this will mean a direct cost reduction impact of USD386,75 per ton of Silicon produced; a big opportunity for the Chinese producers, environmentally and cost wise. Considering that the actual total number of SAF of the main Silicon producers in China are around 295 (Bajoulet, 2015) with the average apparent power of 13,8MVA, and that installed capacity in 2013 was 3,2 million of tons of Silicon and that the utilization factor (yearly basis) of 40 to 50%, this represents 1,6 million tons of Silicon, which consequently means installed capacity of microsilica production around 576 thousand tons per year. Based on the fact that the actual Chinese furnaces that nowadays, 50% of those SAF have proper off gas system to capture the micro silica and produce an average quality level of this by product, the opportunity gap here represents up to 288 thousand tons of Microsilica per year, an opportunity of more than USD57Mio per year for the Chinese Silicon producers, considering USD200/mt of Microsilica. To summarize the opportunities to reduce environmental emissions in Silicon and Ferrosilicon production processes discussed here plus the efficiency increase opportunities, is possible to present the overview in the table sheet below: Process Feeding and Batching system Heat Recovery system Tapping Process Casting Process Losses recycling Environmental Emission Dust/Particulates Energy SiO2, NOx, Cox Heat, Dust Silicon Powder Action/Initiative Dedusting System Heat recovery inst. Secondary off gas installation system

Tapping hood installation Secondary dedusting system Atomization System Opportunity Risk Env. Emissions Energy losses Env. Emissions HS Env. Emissions HSQ Env. Emissions Residues - HSQ Invest. (USD) ROI (years) 2-4 Mio N/A 20-22 Mio 6-7y 3-4 Mio NA 2-3 Mio N/A 7-8Mio 8-9y (pilot) Raw Material Dust/SiO₂/Particula Dedusting System Env. Emissions 2-4 Mio N/A Handling, dedusting tes HS systems Off gas system PCP (pollution control Plant) Microsilica/ Off gas installation Env. Emissions 20-25 Mio 9-10y Heat / HSQ Dust/Particulates Stocking area Heat NO_x, SO_x, Off gas installation Env. Emissions NA NA CO₂, SiO₂, etc. HS Refining Process Al₂O₃, SiO₂, CaO, Top cover usage Env. Emissions 0.5-1 Mio N/A etc. Refining hood installation HSQ Product Handling Particulates, Silicon 4â5 Mio N/A Powder Crushing, Grinding, Silicon Powder Dedusting system Env. Emissions N/A N/A Screening Unit HSQ Operational efficiency increase in Silicon plants Electricity losses CO₂ emissions Increase Si recovery Env. Emissions Economic losses EUR50K for the 1y Diagnostics (plus eventual investment in the Industrial park) Estimates with low accuracy â reference of conceptual engineering phase, +/-60%-70% Base case scenario used in the article â 3 x 27MW Active Power â Submerged Arc Furnaces (Silicon) The author is responsible for the estimates. The authors emphasizes that, the data presented in this study is on the level of conceptual design, based on projects which the authors have been involved from front end loading phases to the execution and operations. The aim of this information is to share experience and give as a reference data base for decision making process in order of magnitude and strategic further decisions. The feasibility of each specific project is related to local conditions such as topography, electricity prices, operational details, raw material used, logistics, labour, suppliers and maturity of the engineering support and technical background of the investor.

27 | Page Road mapping how to reduce the environmental emissions and energy consumption for ferrosilicon and Silicon plant 6 â Conclusion Based on the review of the main environmental emission points in a Silicon and Ferrosilicon Plant, the conclusion is that the opportunities to reduce the emission in the Chinese plants are not only in line of the 13th Strategic 5 year plan (2016-2020), but also there is a huge financial opportunity in terms of increase of the Plants efficiency and emissions reduction as well. The main environmental emission systems discussed on this paper, such as the off gas system for the furnaces, the recycling project for the solid and liquid Silicon wastes, the heat recovery system and the dedusting system for the tapping and casting processes has the return of investment time estimated between 6 and 10 years. Of course this will be highly dependent of the condition of the plants and the approach of the technological supplier for those solutions. What is important to mention is that, the Chinese equipment suppliers have total capacity to develop and delivery such solutions, once one of the 13th Chinese 5 year planning pillar could be implemented properly, the opening up integration, innovation and cooperation development among Chinese regions and worldwide. China Silicon/Ferrosilicon producers, as well as the rest of the world producers; have an important role in terms of the planet environmental protection, due to the level of industrial development that the country have faced in the past decades and also because the protagonist economic importance not only in the Silicon and Ferrosilicon fields, but in the overall ferroalloys development: Is very important also to mention that, for a clear survival question, the high electricity prices locally, the international anti-dumping actions, the increase of the labour costs in China and the raw materials scarcity, is fundamental for the Silicon and Ferrosilicon producers to capitalize the environmental emissions reduction and increase the overall plant efficiencies, pursuing continuously the benchmarking on those fields. The authors would like to state a very important suggestion for further technical studies and implementation in Greenfield Silicon/FeSi as well as brownfield expansions or plant upgrade for a higher â environmentally friendlyâ plant characteristic. Besides the main environmental control systems mentioned in this article, it is important to adopt secondary systems and procedures that would be inside the company's philosophy, such as forestry plant for the entire manufacturing site surrounds, for the purpose of spreading and minimize the impacts of particulate dispersion from the plant, while minimizing the visual and noise impact (green belt concept around the manufacturing site). All those initiatives should be covered within the local regulation, based on norms such as ISO series; this will be important for the sustainability in long term for the improvements, optimization and innovations applied to reduce environmental emissions of the Plant.

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