

Shock Heating of Quartz used in Silicon and Ferrosilicon Production

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Abstract – Six different quartz types used as raw material for Si and FeSi production, were shock heated to 1500 °C in an induction furnace. The amounts of fines produced were measured and compared. The method has been used before on other quartz types. Several parallels were done for each type. The differences between the various quartz types were larger than the differences between the parallels for each type. The standard sample deviation was calculated for each quartz type. It varied from 1.3 wt% to 30.5 wt%. Quartz type D produced the lowest amount of fines, with 3.9-6.6 wt% below 10 mm. Sample F showed the largest disintegration. The amount of fines below 10 mm was around 70 wt%. For silicon and ferrosilicon production the amount of fines produced during shock heating is important for the furnace operation. Together with other high temperature properties of the quartz, the amount of fines will affect the process and hence the product yield and quality. The work presented here is part of a larger project, where the aim is to investigate and identify how and in what way different properties of quartz are affecting the furnace. This knowledge can be used to make decisions when choosing new quartz sources and when operating the furnace, so that the quartz properties are utilized.

INTRODUCTION

Quartz is one of the raw materials used in silicon and ferrosilicon production. Together with different carbon sources such as coal, charcoal and woodchips, quartz is fed to the submerged arc furnace at the top. Three carbon electrodes provides the energy for the process. Raw materials will increase in temperature while they descend, until they reach around 2000 °C. The simplest reaction equation for the process is given in equation 1.

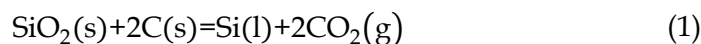


Figure 1 shows an illustration of a process plant. Before the raw materials are fed to the furnace, they are stored, sieved and sometimes washed. After tapping, the liquid silicon is further refined, solidified and afterwards crushed to the desired size. Some of the electrical energy added to the process can be recycled. The byproduct, microsilica, can be collected and sold for suitable applications such as concrete filler. A deeper explanation of the process can be found in Schei et al. (1998).

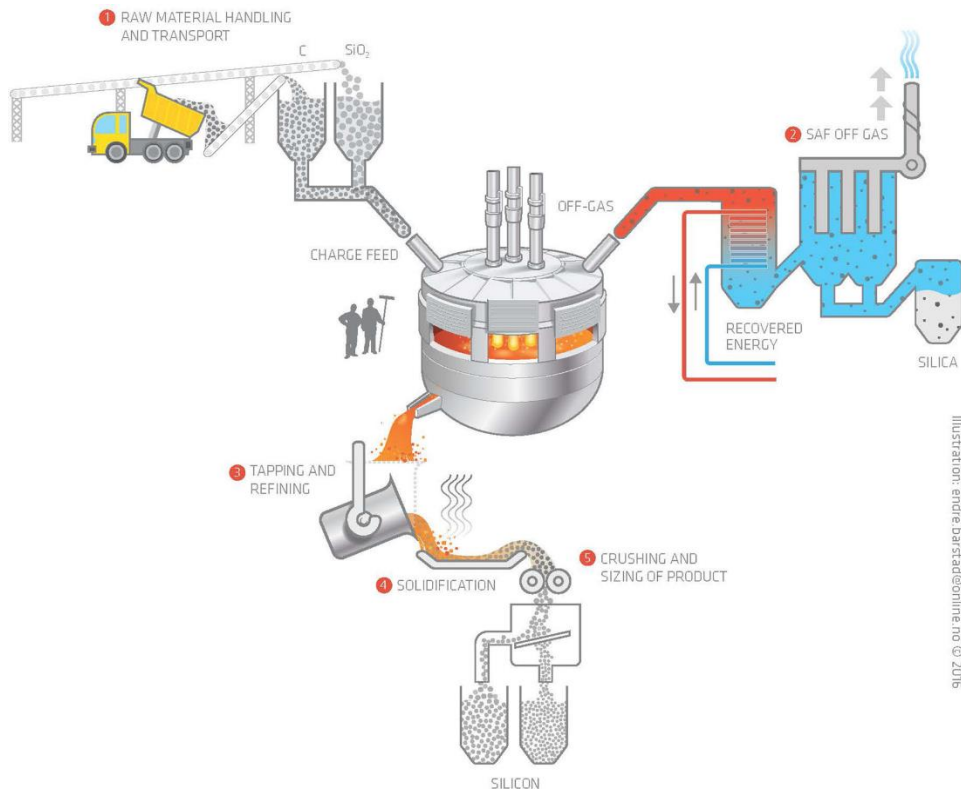
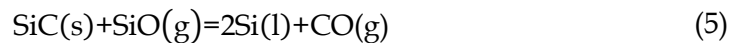
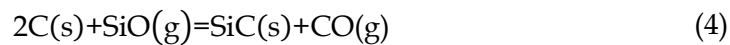
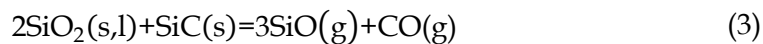


Figure 1: An overview of a silicon production process. The figure is reprinted from Kero et al. (2017) with permission.

In reality the process is much more complex than equation 1 since silicon carbide, SiC, and silicon monoxide, SiO, also are stable components in the furnace environment as described by Schei et al. (1998). For silicon to be produced the temperature has to be above 1811 °C and the partial pressure of SiO has to be above 0.67 atm. SiO₂ can react with both liquid silicon and solid silicon carbide, according to reaction 2 and 3. The SiO gas produced will further react with carbon, according to reaction 4. This is a gas-solid reaction, and the reaction rate will depend on the SiO reactivity of the carbon materials. Silicon will be produced when SiO gas is reacting with SiC, as seen in reaction 5. The liquid product can be tapped from the side of the furnace.



When the raw materials are added to the furnace they will meet a charge top which is 1000-1300 °C (Ringdalen & Tangstad, 2012). Due to this steep temperature gradient from room temperature, the quartz will be shock heated and may disintegrate and produce fines. Ideal lump size for quartz added to the furnace is 10-150 mm (Aasly, 2008). If the amount of fines in the furnace becomes too large, it will have negative effect on the charge permeability. To ensure a good flow of descending raw materials and ascending gas, it is important that the charge is not to compact. Figure 2 illustrates how the gas flow is affected by fines.

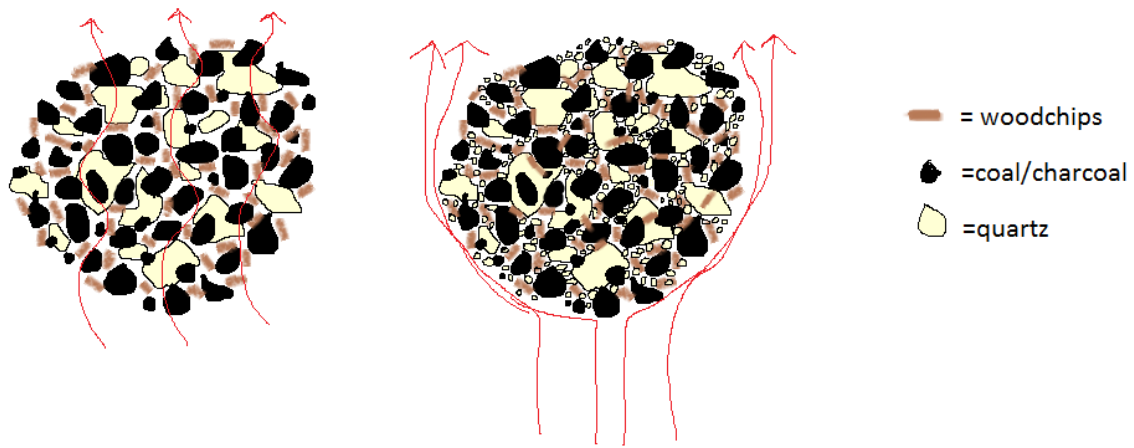


Figure 2: Illustration of gas permeability with varying amount of fines in a furnace. The red arrows illustrates the gas flow.

Other factor such as condensation of SiO and CO gas, softening, and melting properties of quartz could also affect the charge permeability (Ringdalen, 2014). The relative importance of these factors are not fully known. Disintegration of quartz might also affects the condensation reactions in the furnace since the surface area will increase with higher amount of fine particles.

Shock heating experiments have been performed by several researchers (Aasly, 2008) (Bakken & Paulsen, 2013) (Ringdalen, 2014). In figure 3 the results from Ringdalen (2014) and Paulsen and Bakken (2013) are collected. For two samples, Q and T, three parallels were done. It can be seen from figure 3 that there are some variance within a sample. The variance are larger for T than Q. For Q all the parallels fall into the medium group which gave 40-75 wt% < 10mm. There are also large differences in the degree of disintegration from one quartz type to another. The type of quartz added to the submerged arc furnace will then affect the amount of fines in the furnace, and hence the furnace operations.

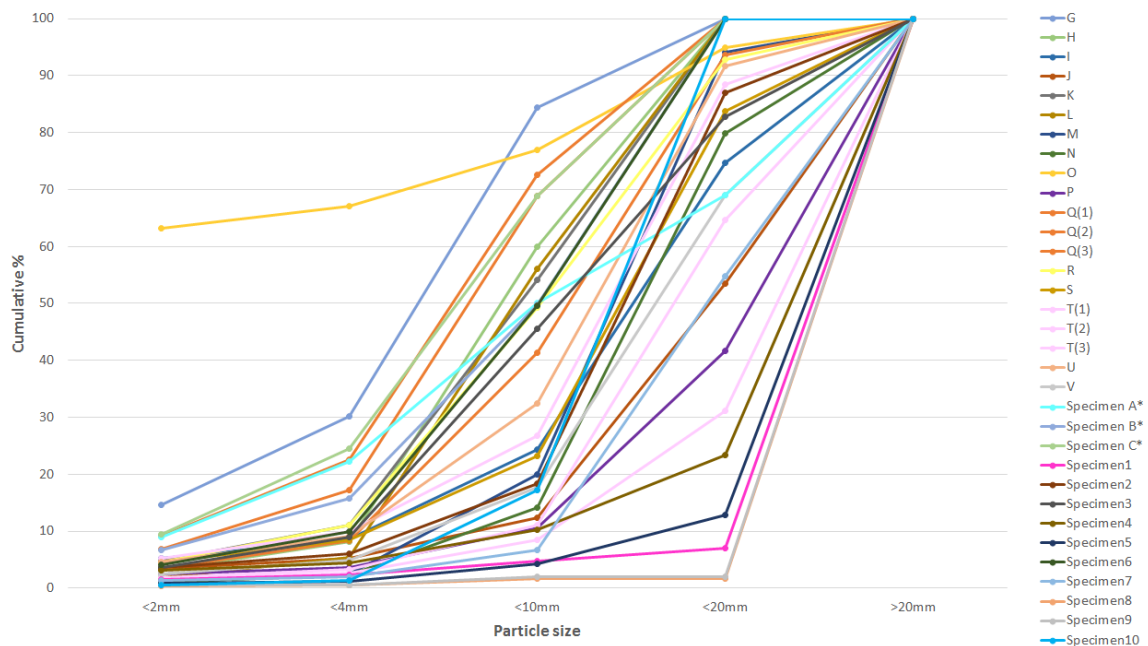


Figure 3: Cumulative percentage of different size fractions of quartz that has been shock heated at 1500 °C. The figure includes results from both Ringdalen (2014) and Paulsen and Bakken (2013).

Paulsen and Bakken (2013) also did the shock heating test at 1300 °C. They found that at 1300 °C specimen C was the most unstable, and specimen 9 was the most stable. At 1500 °C specimen C was still the most unstable, but specimen 8 was the most stable. In general they concluded that the disintegration was significantly greater at 1500 °C than 1300 °C, but there were some exceptions. Specimen 8 disintegrated more at 1300 °C than 1500 °C. However, it must be mentioned that the sample size at 1500 °C was larger than the one at 1300 °C, and this could have affected the result. Figure 4 shows a comparison of the cumulative size distribution of the different samples heated to 1300 and 1500 °C. The figure is based on results from Paulsen and Bakken (2013).

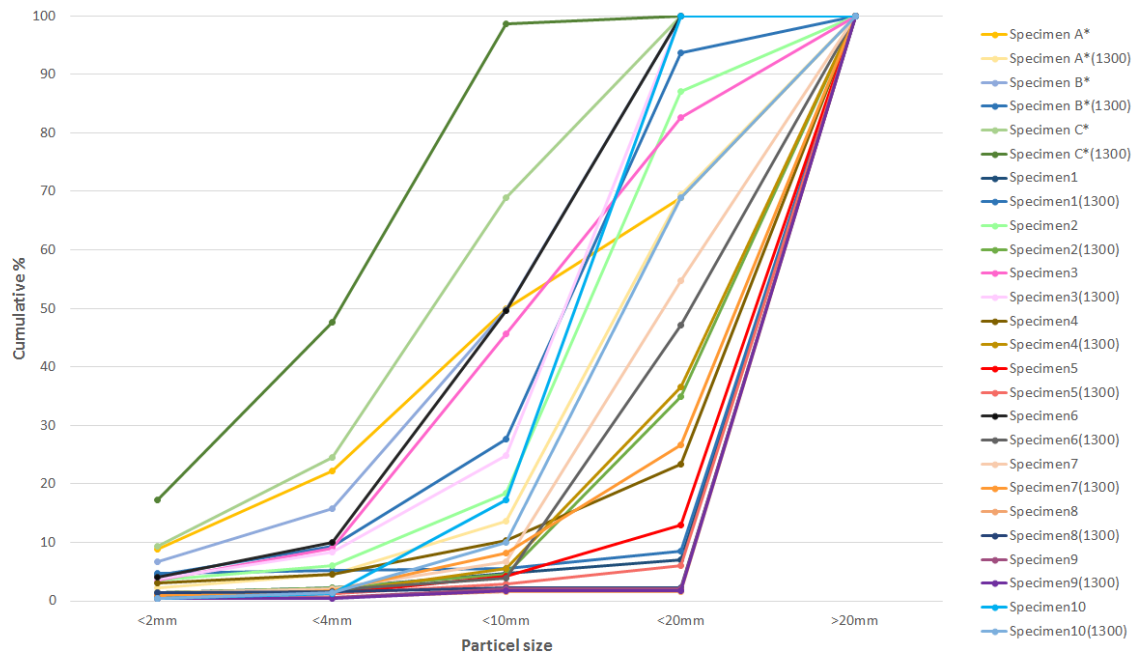


Figure 4: Comparing results from shock heating to 1300 °C and 1500 °C. The figure is based on results from Paulsen and Bakken (2013).

The goal of this study is to determine the disintegration of six different quartz types, including to find the variance within one quartz type. Experiments at 1500 °C will be performed with the same method as used by Ringdalen (2014) and Paulsen and Bakken (2013).

EXPERIMENTAL PROCEDURE

Quartz samples were crushed with a hammer to obtain the desirable size for the experiments, of approximately one 200 g lump. A carbon crucible with height 38 cm and inner diameter 11 cm was heated to 1500 °C in an induction furnace. A thermocouple of type C was used to measure the temperature. The thermocouple was kept inside an alumina tube, which again was placed inside a carbon tube. A piece of Kaalwool was placed on top of the crucible to decrease heat loss. The different quartz samples were placed in the preheated crucible one at a time and kept there for 10 minutes. A sample of quartz type D, prior to heating, can be seen in figure 5. The heated samples were then poured into a cold crucible and cooled in air to room temperature. Figure 6 shows a sample short time after being poured from the hot crucible into the cold one.



Figure 5: A sample of quartz type D, prior to heating. The sample weighs approximately 200 g.



Figure 6: A quartz sample seconds after being poured from the warm crucible in the back at 1500 °C to the crucible in front at room temperature. The quartz is still glowing.

The samples were carefully sieved at 2, 4, 10 and 20 mm after cooling. Each fraction was weighed and recorded. Table 1 below shows the different samples and indicates how many parallels were done for each quartz type. In total 6 different quartz samples used for silicon and ferrosilicon production were tested. The samples were tested in a random order. All sample, except F(2) was approximately 200 g. F(2) were approximately 100 g.

Table 1: Quartz types tested by shock heating. For all the samples, two or three parallels were tested.

Quartz type	No. of parallels
A	3
B	2
C	2
D	3
E	2
F	3

RESULTS AND DISCUSSION

Table 2 shows the percentage of each size group of the quartz samples after shock heating at 1500 °C. Based on these numbers a cumulative representation was made, which can be seen in figure 7. All parallels for each type are marked with a similar color. The difference between each quartz type is larger than the differences between the parallels. The only sample that is left out from figure 7 is sample F(2). This sample was half the size of all the other samples. It also contained some contaminations that glued the fines together. Therefore this sample would not give a representative size distribution for that quartz type. Visual inspection of the samples as they were poured into the cold crucible showed that the quartz had already disintegrated during heating. No further cracking of the samples were observed as the samples cooled.

Industrially the < 10 mm fraction is considered as detrimental fines, and thus sieved out of the charge before added to the furnace. In this paper, < 10 mm particles will also be determined as fines. The total amount of fines after shock heating varies between 3.9 and 75.6 wt% for the different quartz samples tested.

Sample standard deviation was calculated for fines below 10 mm, and is given in table 2. The sample standard deviation is varying between 1.3 wt% and 30.5 wt% for the six quartz types. Sample D and E shows the least variation within the sample, with sample standard deviation of 1.3 % and 1.7 % respectively. On the other end, sample C has a large sample deviation of 30.5 %.

Table 2: Results after shock heating of six different quartz types to 1500 °C. For all the samples several parallels were done. The weight percent for each size fraction are shown.

Quartz	<2 mm [wt%]	2-4 mm [wt%]	4-10 mm [wt%]	Total amount fines, <10 mm	10-20 mm [wt%]	>20 mm [wt%]	Sample standard deviation for fines < 10 mm
A(1)	1.38	1.97	23.18	26.53	73.47	0	
A(2)	2.69	3.24	35.76	41.69	58.31	0	
A(3)	2.22	3.08	17.21	22.51	67.24	10.24	10.1
B(1)	5.91	9.47	50.53	65.91	34.09	0	
B(2)	3.43	4.09	33.35	40.87	59.13	0	17.7
C(1)	11.90	12.83	47.97	72.7	27.30	0	
C(2)	6.00	4.16	19.38	29.54	46.89	23.58	30.5
D(1)	0.49	0.36	3.09	3.94	2.77	93.29	
D(2)	0.73	0.77	3.78	4.59	6.47	88.26	
D(3)	0.97	0.96	4.66	6.59	10.26	83.16	1.3
E(1)	1.60	1.03	9.23	11.86	62.49	25.66	
E(2)	2.08	0.95	6.32	9.35	41.36	49.29	1.7
F(1)	6.12	10.03	57.36	73.51	26.49	0	11.7
F(2)*	5.76	8.74	39.84	54.34	22.71	22.95	
F(3)	5.97	9.72	59.91	75.6	24.39	0	

* The sample was about half the weight of the others.

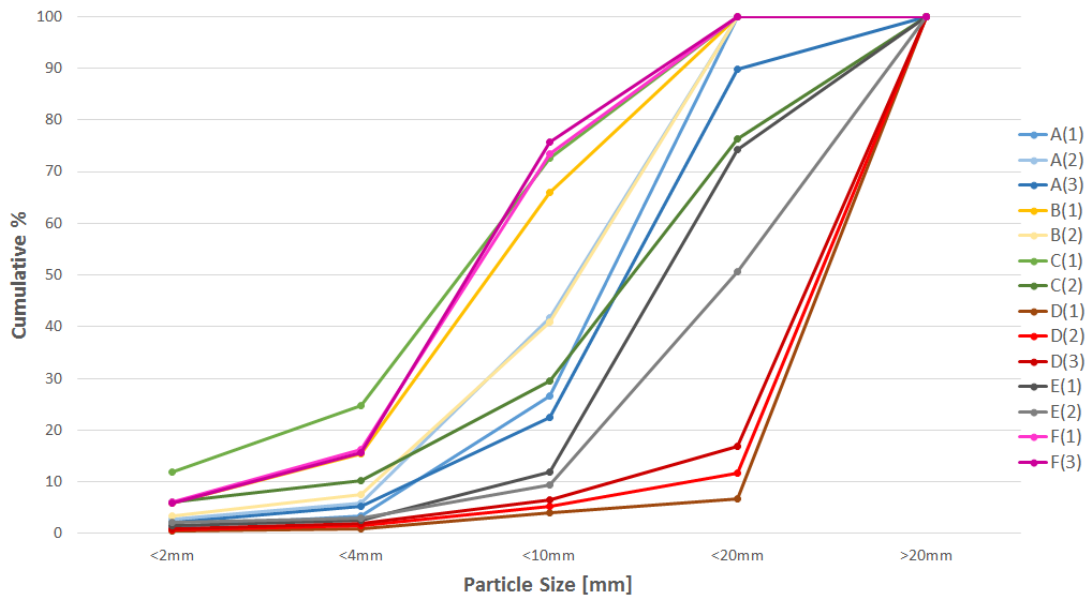


Figure 7: Cumulative size distribution after shock heating different quartz samples to 1500 °C.

In figure 8 the results found in this study are compared with earlier results by Ringdalen (2014) and Paulsen and Bakken (2013). The earlier results are presented as a shaded area in the figure with the results from this study as clear lines. It can be seen that the new experiments fall within the same area as the previous.

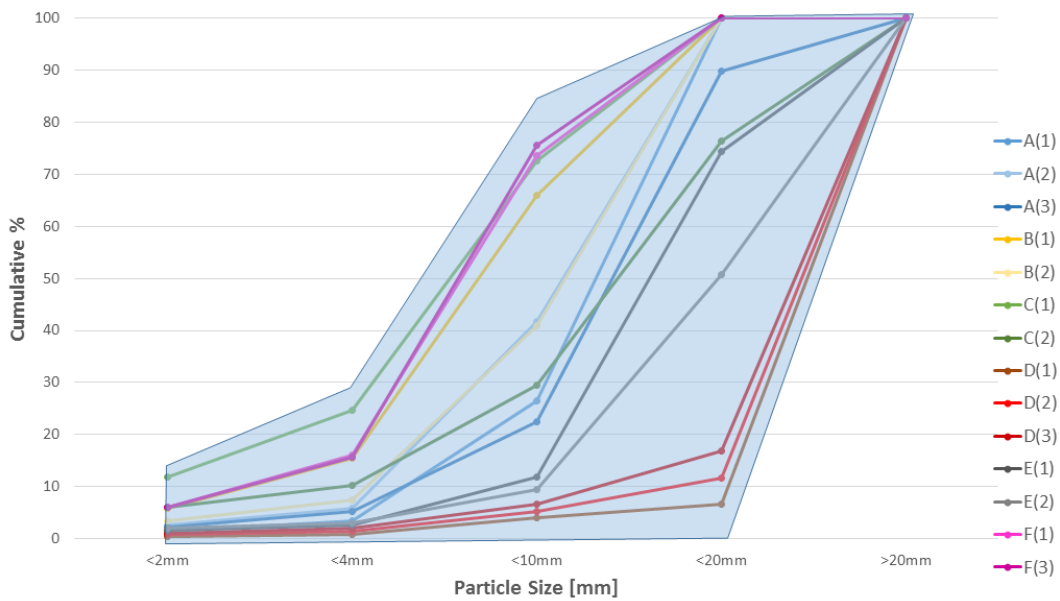


Figure 8: Cumulative representation of different quartz samples after shock heating to 1500 °C. The interval which most of the earlier results fall into, are shown as a shaded area. The earlier results are from Ringdalen (2014) and Paulsen and Bakken (2013).

The following figure shows examples of three quartz types after shock heating to 1500 °C. The variations between the types can be seen clearly. D has not produced as much fines as A or B. From the image it also looks like A has disintegrated more than B.



Figure 9: Three different quartz samples after shock heating at 1500 °C. Quartz type D, A and B shown from left to right.

Figures 10-15 shows each sample after sieving at 2, 4, 10 and 20 mm. It can be seen also from these figures that the differences between the quartz types are larger than the variation between parallels within the same type.

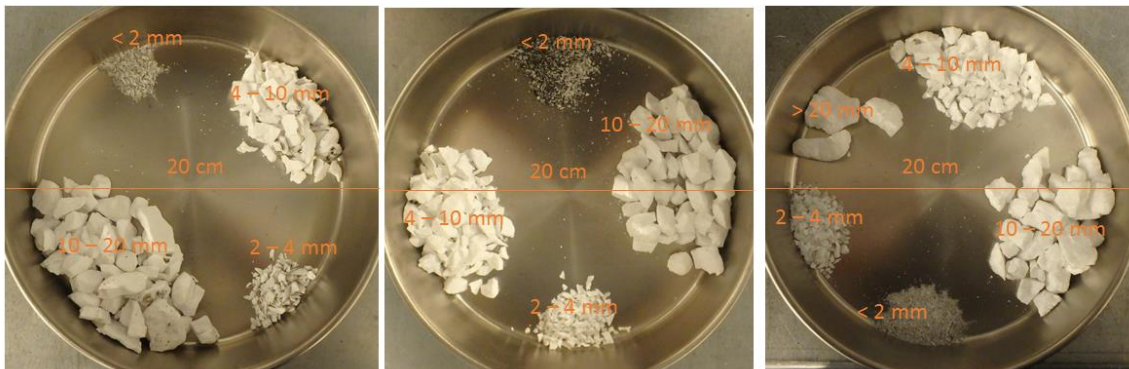


Figure 10: Sample A(1), A(2) and A(3) (from left to right) after shock heating at 1500 °C and sieving.

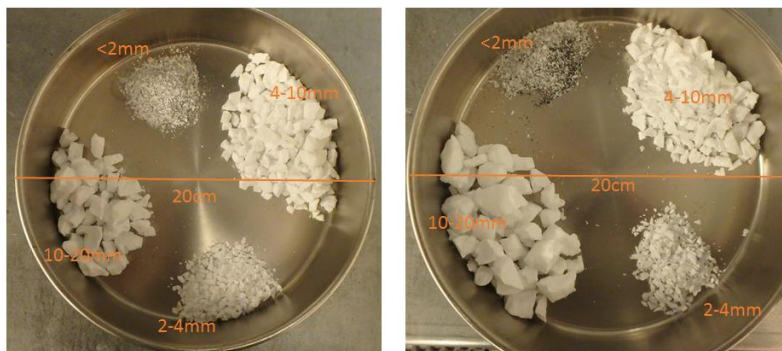


Figure 11: Sample B(1) (left) and B(2) (right) after shock heating at 1500 °C and sieving.

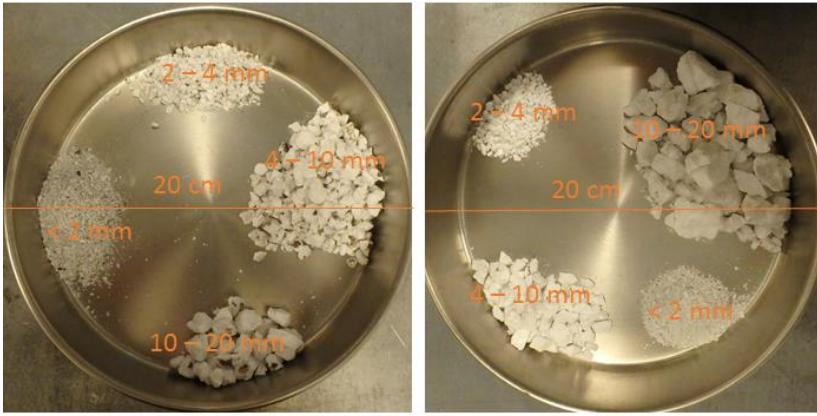


Figure 12: Sample C(1) (left) and C(2) (right) after shock heating at 1500 °C and sieving.

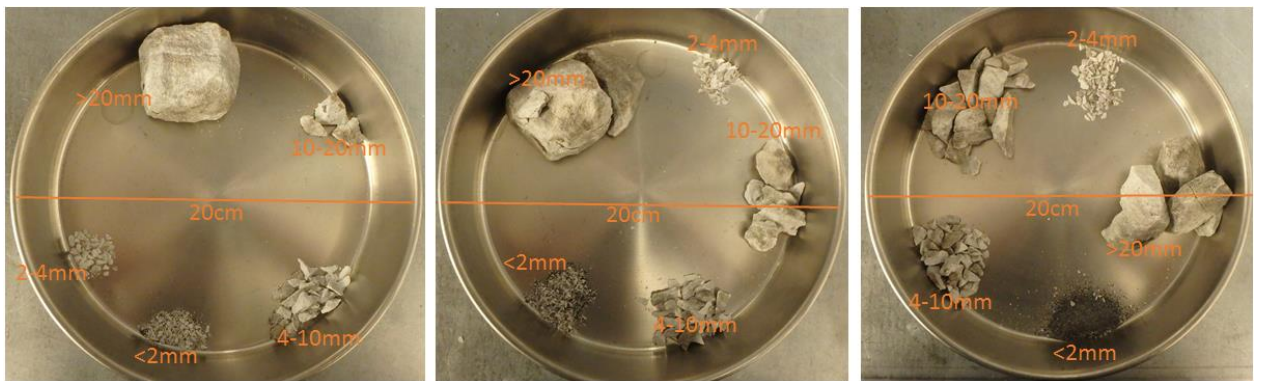


Figure 13: Sample D(1) (left), D(2) (middle) and D(3) (right) after shock heating at 1500 °C and sieving.

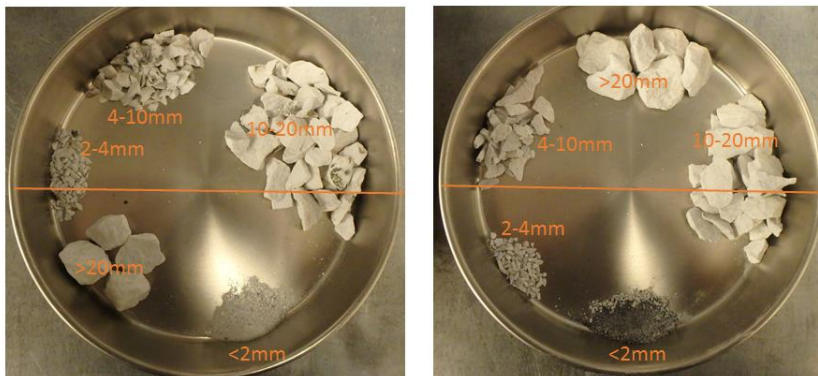


Figure 14: Sample E(1) (left) and E(2) (right) after shock heating at 1500 °C and sieving.

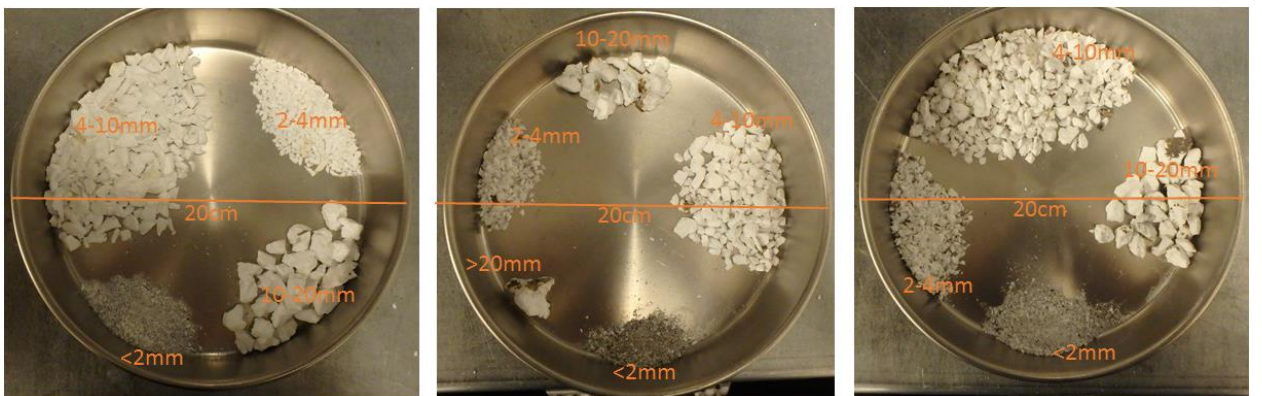


Figure 15: Sample F(1) (left), F(2) (middle) and F(3) (right) after shock heating at 1500 °C and sieving.

As can be seen from figure 10-15 the smallest group with fines below 2 mm often contain some black impurities. These are dust from the carbon crucibles used for heating and cooling. The amount of carbon dust could have affected the weight percent for the fraction below 2 mm. For the larger size fractions, any dust is negligible.

Ringdalen (2014) and Paulsen and Bakken (2013) also found that there are large variations in the fines generation of different quartz types. The amount of fines is assumed to affect the charge permeability in the furnace. Reduced charge permeability has a negative impact on the furnace operation. Therefore, it is desirable to know the amount of fines produced by different quartz types before they are used in industrial scale.

If a quartz lump of 200 g is considered as a perfect sphere, it will have a radius of 26.4 mm. This sphere will have a surface of 8750 mm². When comparing with a disintegrated quartz sample, the total surface will be much larger for the disintegrated sample. The size distribution given in table 3 can be assumed from a sample of original 200 g. The particle radius is assumed to be in the middle of the size interval. Total surface area is calculated for each size group.

Table 3: Size distribution of a 200 g quartz sample after shock heating to 1500 °C. The total surface area are calculated for the sample.

Size group [mm]	Size fractions	Average particle diameter [mm]	Surface area for particle [mm ²]	Number of particles in size group	Total surface area in size group [mm ²]
10-20	36.8	15	707	16	11310
4-10	48.5	7	154	210	32325
2-4	10.1	3	28	546	15435
<2	4.6	1	3	6807	21376
Total surface for sample:					80447

For the above example the total surface area will increase with a factor of approximately 9 when the sample is shock heated. This will affect the reaction area available in the upper part of the furnace, the heat distribution in the raw materials and the charge permeability. For the production it is favorable that the quartz does not start to react in the upper part of the furnace, since the temperature has to be above 1811 °C for Si to be produced. Increased reaction area could increase the possibility for SiO gas to be produced outside the part of the furnace which holds a temperature above 1811 °C. The Si yield will then be lower since more SiO gas is leaving the furnace without being reduced to silicon. Also, the energy distribution might be affected if the rate of reactions in the upper part of the furnace increases. Disintegration will also generate a larger amount of fines that will decrease the permeability in the furnace. An even flow of descending raw materials and ascending gas is necessary for an efficient furnace operation.

CONCLUSION

Disintegration of quartz after shock heating to 1500 °C was tested for 6 different quartz types used for Si and FeSi production. The results show that there are larger variations between the different types than there are between the parallels for each sample. This strengthens the reliability of the method, and shows that differences really exists between quartz types, and not just variations within the same sample.

There are large variations in the fines generation between samples. The sample that had the lowest amount of fines was sample D, with 3.9-6.6 wt% fines. On the other side, sample F and one of the parallels of sample C produced the largest amount of fines, around 70 wt%. Further investigation should be done in order to determine what types of quartz that will disintegrate more readily.

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Karin completed her MSc from the Norwegian University of Science and Technology spring 2016, and started her PhD work the following fall. Her work, both in the master thesis and PhD thesis, are focused around the high temperature properties of quartz used in silicon and ferrosilicon production. She has held several presentations of her work, included TMS in 2016 and at PhD Grand Prix at NTNU in 2017.
