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WATER GRANULATION OF FERROSILICON AND SILICON METAL

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ABSTRACT

Today the market is expanding for water granulated qualities of both silicon metal and ferrosilicon. A growing number of silicone producers find that water granulated silicon metal is favourable in their chemical process. More and more consumers of ferrosilicon are experiencing less environmental problems by switching to water granulated qualities which in addition often are raising the yield.
Fesil AS (the new name of Ila og Lilleby Smelteverker AS from June 1st 1995) has been a pioneer within granulation of both ferrosilicon and silicon metal. This paper tells about the development of water granulation done by Fesil AS.

WHY GRANULATION OF FERROSILICON ?

In the water granulation process the ferrosilicon alloy is cast directly in water to the final shape required by the consumer. Ferrosilicon granules need no further crushing and save the losses of dust created during crushing. It is very favourable that the quick cooling gives ferrosilicon granules a finer and stronger structure/surface than normal casting and crushing of ferrosilicon.

This strong granule structure means that less fines/dust are created during transportation to the consumer and by his own handling. Many consumers of ferrosilicon have experienced much less environmental problems after switching to a granulated quality. It is therefore no surprise that many of them have reported a higher yield with granulated ferrosilicon.

Granulated ferrosilicon is a possible replacement for ferrosilicon sized up to 20-30 mm because it seems very difficult to produce a main part of the granules coarser than 20 mm.

WHY GRANULATION OF SILICON METAL ?

Granulated silicon metal is developed for the chemical silicone industry which is consuming more than 40 % of the worlds total silicon production. The silicon metal is granulated to get the wanted structure inside each silicon granule which is ground down to 100-200 μm to be processed in the Direct Process, a fluid bed where silicon reacts with methyl chloride.
The structure of normal cast silicon and water granulated silicon is shown in Figure 1 and 2.

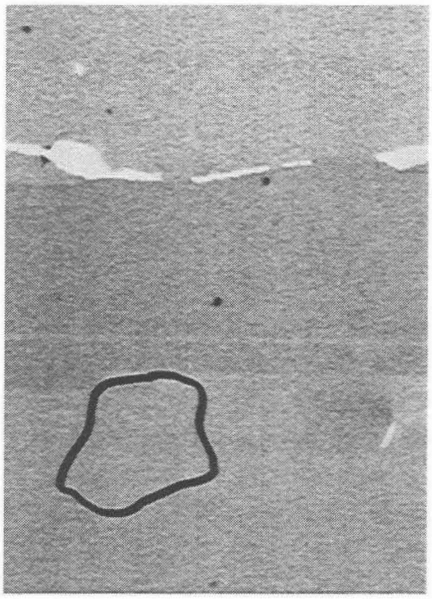

Figure 1. Normal Cast Silicon.
Magnification 100x.

Figure 2. Water Granulated Silicon
Magnification 100x.

Explanations to figure 1 and 2 :

Light/Dark Grey area	:	Silicon
White area	:	Intermetallics (Fe,Al,Ca, etc. not soluble in solid silicon)
Black area	:	Air as pores or cracks
Figure	:	A typical particle in Direct Process: Size 100-200 μm.

Figure 1 shows normal cast silicon. The distance between the thick layers of intermetallics may be more than 500 μm. Typical particles in Direct Process measure only 100-200 μm. When crushing normal cast silicon, the thick layers of intermetallics will therefore be highly unevenly distributed between the particles. But in the Direct Process the productivity is controlled by the reaction between silicon, intermetallics and the catalytic system on the surface on each single particle. Uneven distribution of intermetallics may cause problems.

Figure 2 shows water granulated silicon where quick cooling is causing intermetallics to be closely distributed in thin layers. When crushing granulated silicon, the intermetallics will be evenly distributed between the particles. The surface of most particles will be stained with favourable intermetallics giving a big surface of highly activated silicon.

Wacker-Chemie Gmbh is the biggest German producer of silicones. Dr. Pachaly[1], who is the source for the explanation given here, describes how Wacker uses microscope, video camera, PC and image analysis program to describe the structure. This method gives a quantitative structure index number called QF, examples in Table 1.

TABLE 1: Wackers [1] Structure Index Number as a Function of Solidification process

Solidification Process	QF (Structure index)
Very slow cooling of silicon in big lumps gives big crystals	0.1 - 1
Mould casting of silicon in different thickness'	5 - 10
Water granulation of silicon to sizes between 5 and 15 mm	20 - 40
Air-beam granulation of silicon to 2 - 3 mm	40 - 50
Atomisation of silicon in an inert gas to < 1 mm	60 - 65

To day Wacker assume QF = 25 - 35 to be optimal in their process. This seems most logical to achieve by water granulation, but 3-10 mm air-beam granulation may be an alternative.

In 1992 Wacker challenged Fesil to produce silicon with the wanted QF. For some years winds had whispered about test granulation of silicon around the world, but no well proven technology was available in the market. We therefore started to do some small scale testing of different casting methods, but soon we decided to go deeper into water granulation.

TECHNOLOGY FOR GRANULATION OF FERROSILICON AND SILICON

Co-Operation between Uddeholm and Elkem on Ferrosilicon

Uddeholm, the leading supplier of plants for metal granulation, worked a short time together with Elkem on granulation of ferrosilicon. Soon Uddeholm left this project because Elkem alone wanted to develop granulation of ferrosilicon to an industrial process. Specially in the beginning Elkem had many explosions, but now for many years Elkems granulated ferrosilicon (Gransil) has been a big success in the market.

Uddeholm

Figure 3 illustrates Uddeholms technology: Metal is poured into a tundish(17) with a casting hole(18) located exactly over an impact element(8), a round brick with a flat top, above the surface of water. When liquid metal(19) hits the brick(8), it is disintegrated into drops being spread over the water tank. Specially for slow sinking silicon with a high heat content (=2.3 times that of iron) Uddeholm says it is useful to move the brick(8) up/down by hydraulics(9) to get the silicon more evenly distributed over the water tank.

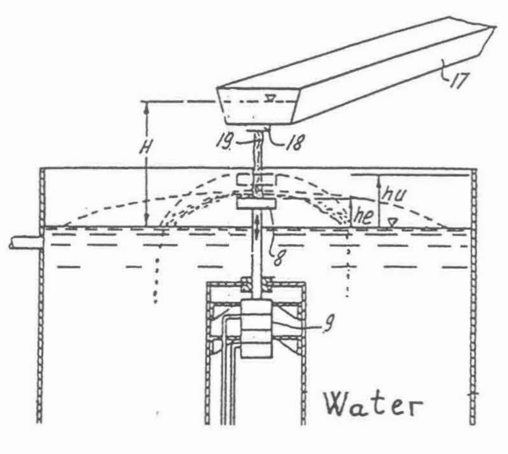

FIG. 3. Uddeholm Eur. Pat. Appl.[2]

Figure 4 shows Fesils calculation of the variations in the drop formation energy over one brick stroke sequence (=0.4 sec) :
The first half of the upward stroke Uddeholm are accelerating the brick up to 125 cm/sec to achieve max. drop formation energy (100 %). The brick is then gradually retarded on its way to the top position. Here the drop formation energy is only 40 % because the energy of free falling metal are at its mini- mum when the brick stops. The downward stroke of the brick takes only 0,04 sec which is quicker than the metal falls.

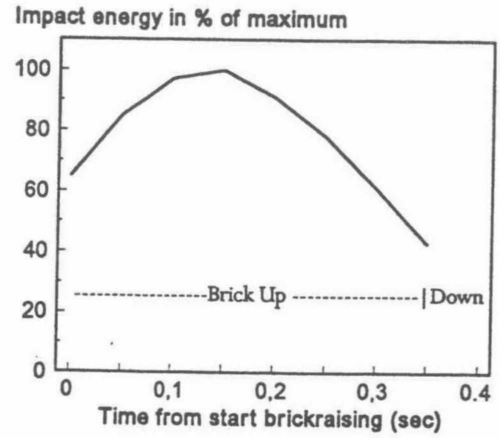

FIG. 4. Calculation of impact energy

Uddeholms brick stroking arrangement seems to create a favourable distribution of the metal. But one side effect is the variation pattern in drop formation energy demonstrated in figure 4. Our experiences indicate that variations between 40 and 100 % will most probably give the silicon granules a very wide size distribution. The importance of the size distribution of silicon granules will be more clear when a normal market for granules is established.

Fesils Own Experiences

More than 20 years ago our plant Lilleby Metall tried full scale granulation of ferrosilicon. But the first ladle created a big bang and the granulation idea was mentally buried for years.

Elkems success with granulated ferrosilicon inspired Hafslund Metall in 1989 to start developing their own granulation process for ferrosilicon. In 1992 Hafslunds full scale plant successfully came in operation. By chance it was the same year that Wacker asked Fesil for granulated silicon for the first time. We therefore decided to investigate if it could be possible to expand our technology to include even silicon.

CRITICAL FACTORS IN A SILICON ALLOY GRANULATION PLANT

Our natural basement for expanding ferrosilicon technology to include even silicon was to study the most critical factors and most important differences between those two metals.

Removal of Heat - Vapour Explosions

About ten years ago Uddeholm printed a brochure saying how fast drops of ferrosilicon and silicon are freezing when sinking in water: During sinking the first meter in water Uddeholm assumed that about 95 % of a silicon drop and about 80 % of a ferrosilicon drop will be frozen. If this should happen to be true for silicon, it would be a challenge to handle very concentrated heat transfer from freezing silicon in the upper meter of the granulation tank.

We let liquid silicon drops fall down a waterfilled vertical tube. Drop of liquid silicon could sink more than 2 meters in water before being frozen all through which was proved from the formation of visible bubbles of hydrogen gas from the bottom of the tube: Important knowledge telling us that the cooling was slower than Uddeholm assumed.

Oxyhydrogen Gas - Detonating Gas

Granulation of both ferrosilicon and silicon is releasing hydrogen :

$$Si\,(l) + H_2O(g) = SiO_2(s) + H_2(g) \qquad (1)$$

This exoterm reaction is kinetically controlled, and can not be totally avoided. It will be influenced by silicon drop size/analysis/temperature and water properties. It is important to prevent the hydrogen gas to mix up with air to a detonating gas in a place where this mix may be ignited by a hot drop of silicon. When this happen, you hear a sharp crack. This is normally harmless, but it is very important to construct the granulation plant in a way that does not allow this detonating gas to accumulate which may lead to a serious explosion.

Solidification of Ferrosilicon - Importance of Analysis

Ferrosilicon is freezing between 1400°C and 1200°C through precipitation of solid silicon in a melt of ferrosilicon with a rising content of iron. During freezing a silicon crystal are expanding its volume about 10 %. When silicon precipitation is finished at 1200°C, the remaining melt ($FeSi_2$) is occupying 25 % of the total volume. But as long as silicon are freezing inside this liquid volume, it is reason to believe that the 10 % expansion of silicon will only have a minor impact on the surface of the ferrosilicon drop. The freezing of $FeSi_2$ at 1200°C expands the volume by only 0.6 %, considerably less than 10 % for silicon.

On the other hand we know that granulation of ferrosilicon, high in calcium and aluminium, will be heavily disturbed because especially calcium then will react with water prior to silicon. The reaction is like equation (1) when silicon are replaced by calcium and aluminium. Therefore, there are analytical restrictions with respect to the calcium and aluminium content of liquid ferrosilicon prior to granulation.

Solidification of Silicon - Importance of Analysis

Silicon metal is only containing a minor amount of iron, aluminium and calcium which in the state of intermetallics only are occupying about 1 % of the total volume when the silicon is freezing at 1400°C. It is reason to believe that this minor 1% volume, compared to the 10 % with ferrosilicon, must give a quite different protection when silicon metal is freezing.

This may explain why it seems difficult to make coarse granules out of silicon. Our experience is that big silicon granules often gets its surface broken like a volcano when its liquid core is freezing and expanding 10 % at the same time.

Analyses of silicon are also of great importance to the operation of a granulation plant, even if the calcium and aluminium values are lower than what can be tolerated when granulating ferrosilicon. Again it is reason to believe that the very limited amount of intermetallics is important. Tuset[3] has presented equilibrium diagrams for silicon refining which shows that even small changes in calcium/aluminium content of silicon may affect the important oxide surface protecting both silicon and intermetallics from further oxidation: The oxide surface may change from liquid to solid state at a given temperature, from a tough to a crispy slag and even from a density lower than for silicon to a density higher than silicon.

ILS have experienced that analysis of silicon are of importance, but we have not tested out the more troublesome analyses in a systematic way suitable for presentation.

HOLLA GRANULATION PLANT FOR SILICON METAL

After many small scale tests a slim full scale plant was erected at the end of 1993. We experienced some minor and solvable problems during full scale test operation, but to granulate silicon seemed to be possible in a safe and economical way. A small tonnage of granules satisfied our test customer, and the plant was completed in 1994. We can not here describe the practical arrangement between the ladle and the water because this part of the process is under evaluation for patent application(s).

Granules are continuously transported from the bottom of the granulation tank to a special dewatering unit followed by batchdrying. Dry granules are screened into two fractions. Less than 0.5 % of the total input are lost as sludge with the water. Capacity during granulation is 150-250 kg/min, but intermittent supply of silicon limits capacity to about 250 tons/week.

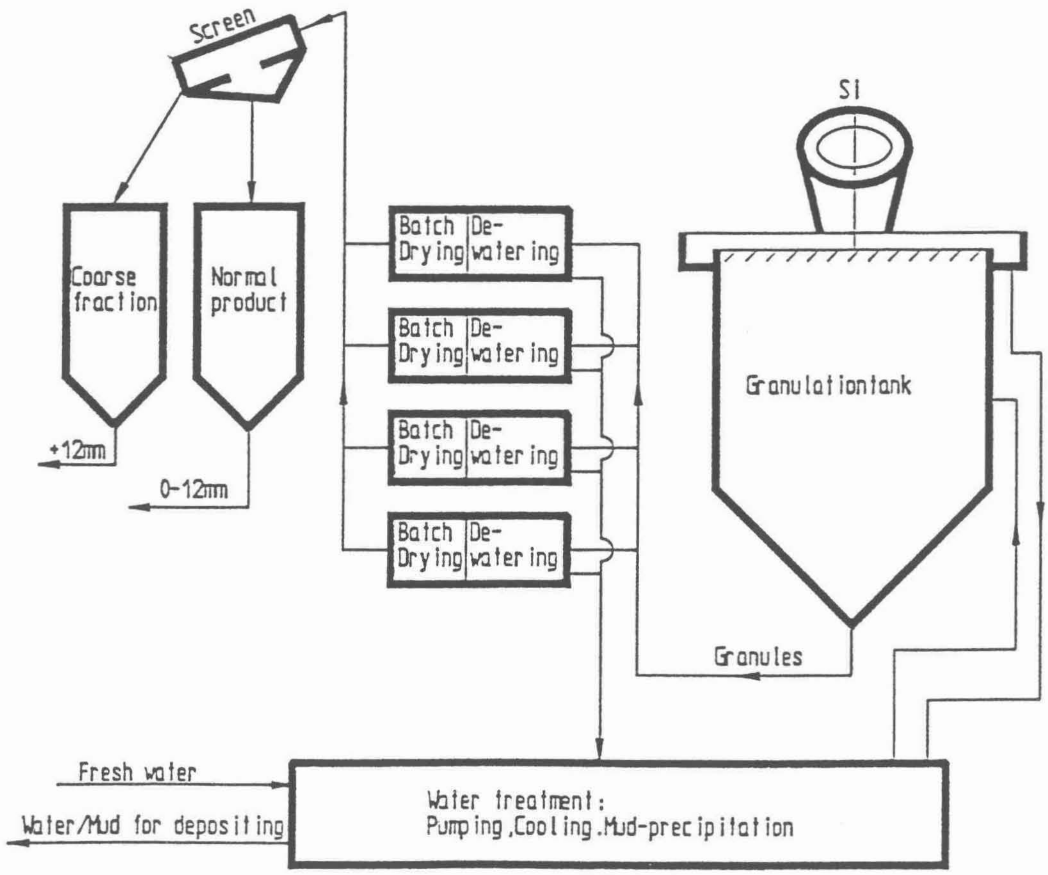

FIG. 5. Sketch over the Holla Granulation Plant for Silicon

HAFSLUND GRANULATION PLANT FOR FERROSILICON

The design of the Hafslund granulation plant is in many aspects similar to the Hollas plant. At Hafslund however, the continuos stream of ferrosilicon granules is directly wet screened into the fractions -1mm, 1-5mm and 5-25 mm. The capacity is about 600 tons ferrosilicon per week. During the three years of operation the plant has been performing very well both with respect to the quality of products as well as the safety level of the operation.

GRANULATED PRODUCTS

Table 2 shows the total granule sizing before screening. Ferrosilicon is on purpose granulated much coarser than silicon. The amount of - 1 mm is low and at the same level. Granulation losses to the water are therefore very limited.

TABLE 2 : Sizing of Products

Fractions mm	Ferro-silicon-sizing %	Silicon metal sizing %
+25	0.3	0
20 - 25	2	0
16 - 20	8	0
10 - 16	38	1.5
5 - 10	34	33
3 - 5	7	45
1 - 3	9.5	18
- 1	1.2	1.2
Sum	100	100

Granulation gives lower pouring speed than normal casting. Some more ferrosilicon/silicon are therefore freezing in the ladle/runner/tundish, but most of it is recoverable. On the other hand granulation are avoiding crushing losses. In the long run, we believe that the granulation process is superior to the conventional casting/crushing/screening route with respect to overall metal yield.

Silicon metal analysis is very stable. Only fractions smaller than 0.7 mm show a rising content of intermetallics, but those fractions are limited to about 1 % of the total input. The relations Fe/Al/Ca in fine fractions are very stable, which prove that the fines are upconcentrated on intermetallics and not on oxides from a Ca/Al-refining.

CONCLUSION

Producers of silicon for the silicone industry are today facing a possible development towards silicon granules. But it is too early to know how big this granule market will grow. Neither ferrosilicon producers know how many steelplants will switch over to environmentally friendly granulated ferrosilicon which even may give better yield. Fesil has developed its own processes for safe and economical granulation of both ferrosilicon and silicon metal, and we feel prepared for this interesting development.

ACKNOWLEDGEMENTS

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