

standard. The lake region alone produced beets, which were uniformly of a high grade, when all the requirements of a good beet were taken into account.

4. Topographical features of land are of importance in determining a suitable location for a sugar factory. It is well known that beets grown in the shade are worthless for the manufacture of sugar. In view of this fact it would seem almost superfluous to say that a partial obstruction of the direct rays of the sun daily would cause the production of a crop of beets of lower sugar content than would be the case if such obstruction did not occur. Consequently level tracts of land, where on clear days the plants are exposed to the direct rays of the sun from morning to night, must be better adapted to beet culture than deep valleys, especially if they are narrow and skirted by hills or mountains, and if in addition their general course is from north to south.

The writer is convinced that the variation in the composition of beets grown in the same sections of the country, having a diversified topography, is due in a great measure to the injudicious selection of the fields in this respect.

There are other factors which enter into the successful inauguration of the proposed new beet-sugar industry in this country, but, as a guide to the selection of the most favorable localities for its permanent establishment, the matter of light should receive due consideration.

COMMERCIAL IRON SILICIDES WITH A HIGH PERCENTAGE OF SILICON: THEIR PROPERTIES, MANUFACTURE, AND USES.

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IRON silicides containing about eleven to thirteen per cent. silicon have, for some years, been made in blast-furnaces, and have been successfully introduced in the manufacture of iron and steel. It has been found impracticable to much increase the amount of silicon by the blast-furnace process. This can, however, be successfully done by changing the process and making use of the great heat of the electric furnace. I have made, in the electric furnace, silicon-iron alloys containing from

twelve to forty-six per cent. silicon. In alloys up to 46.5 per cent. silicon, and most probably in those up to fifty per cent. silicon, the iron and the silicon are chemically combined; *i. e.*, there is no free silicon and no free iron present. If more than fifty per cent. silicon is forced into the iron, the excess crystallizes out in small black crystals. This article deals only with silicides containing twenty-five to fifty per cent. of silicon.

COMPOSITION.

Silicides of from twenty-five to fifty per cent. silicon seem to consist of a mixture of two distinct compounds between iron and silicon; compound *a*, which contains twenty-five per cent., and compound *b*, which contains fifty per cent. silicon. These compounds are represented by the chemical formulas Fe_3Si_2 and FeSi_2 . Both these compounds were obtained pure enough for analysis. When iron silicides with about twenty-five to twenty-eight per cent. of silicon are allowed to cool slowly from the liquid condition, compound *a* will crystallize out in very well-developed crystals, some of which will be as large as one-half inch to the side. These crystals have never been determined crystallographically. They have, among others, well-developed tetrahedral faces. These crystals are best obtained from an alloy containing from one to two per cent. silicon above twenty-five per cent. It is probable that some iron-silicon compound containing less than twenty-five per cent. silicon hinders the crystallization of the compound Fe_3Si_2 .¹ Crystals obtained at various times and in different furnaces contained:

	1.	2.	3.	Composition of Fe_3Si_2 .
	Per cent.	Per cent.	Per cent.	Per cent.
Iron	74.75	75.89	75.00
Silicon	25.17	25.30	24.48	25.00

To isolate the compound *b*, I make use of the fact that acids attack the silicide faster the lower the content of silicon. I used a silicide containing about thirty-nine per cent. silicon, and which, according to my views, contains fifty-six per cent. of compound *b*, and forty-four per cent. of the compound *a*.

The acid used was hydrofluoric acid. This acid attacks both

¹A most beautiful specimen of these crystals can be seen at the New York office of the Willson Aluminum Co. It is a piece of silicide of fifteen inches in diameter, on one side entirely composed of these crystals, some being among the best developed that were ever produced.

compounds rather easily, and in order to obtain any residue I had to work carefully and with moderation. The finely pulverized silicide was suspended in water and the acid added in successive small amounts. By thorough cooling, a too violent reaction was prevented. The acid added was not sufficient to dissolve the whole of the silicide. The residues, which were thus obtained, contain :

	1.	2.	3.	Composition of FeSi ₂ . Per cent.
	Per cent.	Per cent.	Per cent.	
Iron.....	50.56	52.24	50.00
Silicon.....	49.71	48.26	49.35	50.00

The yield of residue was about twenty per cent. of the amount taken. Compound *b*, thus obtained, forms a gray crystalline powder quite unmagnetic.

I have obtained in the furnace an alloy containing: Iron 53.76 per cent., and silicon 46.22 per cent., which corresponds to a content of 84.88 per cent., of the compound *b*. This alloy was gray and crystalline, and could be easily pulverized.

Hahn has described an iron silicide of fifty per cent. silicon, which he produced in minute quantities by treating a twenty per cent. silicon alloy with hydrofluoric acid. He describes this compound as insoluble in hydrofluoric acid; hence it is different from that which is found in my silicides. It was produced in an entirely different manner.

Among the combinations more likely to be present in my silicides, might be the compound FeSi with 33.3 per cent. silicon. Such a compound has been described by Hahn and by Fremy. It is not easy to show with certainty that such a compound is not present in these silicides, where we have to deal with a mixture of compounds having similar properties. It seems probable that this compound does not exist in my silicides. An alloy containing 31.4 per cent. silicon was taken. If the compound of 33.3 per cent. silicon existed, it would be present especially in this alloy in large quantities. We might expect this compound to contain 22.9 per cent. of compound *a*, of twenty-five per cent. silicon, and 77.1 per cent. of the compound with 33.3 per cent. silicon. On the other hand, if the compound of 33.3 per cent. silicon is not present the alloy would contain 74.4 per cent. of compound *a* of 25 per cent. silicon, and 25.6 per cent.

of compound *b* of fifty per cent. silicon. In the first case there is a great excess of the 33.3 per cent. compound, and we might expect that compound *a* could not form well-developed crystals. In the second case compound *a* being far in excess it would probably yield better-developed and larger crystals. I have pulverized the alloy of 31.4 per cent. silicon, to forty mesh sieve, and attacked it with such an amount of hydrofluoric acid as is not sufficient to dissolve the whole mass.

If now the first case be true, the compound *a* will be probably more soluble in acids than the other compound, which contains more silicon. This is a general rule among silicides. Compound *a* is only present in small amounts and is probably not present in large, well-developed crystals. The result will be that compound *a* will be quite or nearly dissolved, and some of the compound of 33.3 per cent. silicon will remain in a more or less pure condition. The residue will then contain more silicon than the original alloy.

In the second case there is a chance for a larger percentage of compound *b* than of compound *a* to be dissolved; for although the latter be more soluble in acids, it is present in large excess and probably in much larger and better-developed crystals than the compound *b*. If a larger proportion of compound *b* than of compound *a* should be dissolved, the residue will contain less silicon than the original alloy.

Acting on the coarsely powdered alloy of 31.4 per cent., silicon was found to produce a residue which contained less silicon than the original.

	Original alloy. Per cent.	Residue. Per cent.
Silicon.....	31.4	30.2

This result renders the presence of a compound FeSi doubtful.

PROPERTIES.

Iron silicides are invariably crystalline, and are white or gray in color. Silicide with from twenty-five to thirty per cent. silicon takes a fine polish, when it more or less resembles silver, although somewhat darker. The higher-grade silicides are the darker in color. The melting-point rises with the percentage of silicon. Silicide of twenty-six per cent. silicon can be melted in the crucible of a brass furnace, but takes a higher temperature

than brass. Silicide of thirty-two per cent. silicon cannot be melted that way. This latter can be melted in a crucible by using a good blast. The silicides containing more silicon could be successfully melted only in an electric furnace. These silicides should not be molten in a blast cupola. The silicon burns as easy or easier than the coke, and the molten metal will contain considerably less silicon than the original. A lot sent to a foundry and treated in a cupola lost five per cent. silicon out of twenty-seven per cent. If such partly oxidized metal is cast, it will often form a coating of a gelatinous silica in the mold. The latter is weakly transparent and elastic to quite a degree. I saw similar silica exhibited in the Carborundum Works at Niagara Falls.

Lower-grade silicides cast very well with sharp outlines and corners. When the amount of silicon is increased, the castings show a tendency to crack when cooling. The silicides of thirty-four to forty per cent. silicon usually form blow-holes besides cracking, when the castings cool. When the higher-grade silicides are cooled very slowly the tendency to crack is lessened. All these silicides are but slightly magnetic, and those with over thirty per cent. silicon are quite non-magnetic, which well shows that there is no free iron in the alloy. Their specific gravity falls with the percentage of silicon.

	Alloy of 12 per cent. silicon.	Alloy of 25 per cent. silicon.	Alloy of 46 per cent. silicon.
Specific gravity at 20° C.	6.8	6.36	4.85

These alloys conduct electricity easily, and are very hard. They are brittle, the more so when the percentage of silicon increases. They are unalterable in air or in water. Acids attack them very little, especially if they are not pulverized. Hydrofluoric acid forms an exception, for it easily dissolves all these alloys. Acid oxidizing agents attack these silicides less, the more silicon there is present. In order to obtain some idea of the rate at which the solubility in these agents varies with the percentage of silicon, three samples, *a*, *b*, and *c*, were ground so that they easily pass through a 100-mesh sieve. Two grams of each were treated with the reagent at summer temperature, side by side for two days, stirring frequently.

	50 cc. aqua regia 1 HNO ₃ to 3 HCl. Per cent. dissolved.	100 cc. saturated chlo- rine water. Per cent. dissolved.
<i>a</i> with 13 per cent. silicon	66.84	5.88
<i>b</i> " 25 " " "	9.86
<i>c</i> " 46 " " "	0.76	0.83

Toward alkalis the low grades are more resistant than the high grades. Fifty cc. of a twenty per cent. solution of caustic soda dissolved in two days from two grams of the ground silicide :

<i>a</i> with 13 per cent. silicon,	3.96	per cent. dissolved.
<i>c</i> " 46 " " "	9.68	" " " "

Silicides made at Holcomb Rock contained :

	I. Per cent.	II. Per cent.
Silicon.....	26.35	36.56
Manganese.....	trace	0.31
Sulphur.....	trace	trace
Phosphorus.....	trace	trace
Titanium.....	0.94
Carbon.....	none	none

This alloy is thus shown to be of great purity.

Pieces of iron silicide are often found in calcium carbide, especially in carbide made from inferior materials. I found in such pieces from twelve to forty-five per cent. silicon. Any attempt to write chemical formulas for the material of such pieces must fail. They are mixtures of the same nature as those obtained in quantity.

MANUFACTURE.

The raw materials, which are commonly used in the works of the Willson Aluminium Co., are a good iron ore, river sand, and any kind of coke. The river sand contains some manganese and titanium. The quality of the iron ore can be materially reduced so long as the chief impurity is silica. In fact, for many reasons such an ore is preferable. After trying many fluxes, they were entirely abandoned, for they always reduced the output.

The materials are finely ground with the exception of the silica which should be of the size of coarse sand, on account of its volatilizing easily; and being very light, it is readily carried away by the draft of the furnace. At the temperature that exists in the electric furnace, the carbon monoxide does not act

as a reducing agent, and it is the solid coke particles that do the reducing. For this reason the mixing must be thorough and the ingredients must be finely ground.

We use at Holcomb Rock Works a continuous furnace of my own design. It is fed at the top and tapped at the bottom. These furnaces are run one week or in fact any length of time, and they can be cleaned and made ready for use again in a few hours. We make, so far, iron silicide in furnaces of only about 150 electrical horse-power, but by enlarging the furnace, we can easily use 1000 horse-power or more in one furnace, which will materially reduce the cost. Our furnaces give little dust and that only when they are opened. This is a great advantage, for the fine silica dust is very objectionable. I have seen this dust settle two inches deep all over the room from an open furnace.

During the operation the alloy runs to the bottom of the furnace, where it collects in a pool and is tapped at regular intervals. There is only little slag, if the materials are mixed in proper proportions. The metal which runs out is very free of enclosed slag. It comes out white and the tapping can be seen for quite a distance if windows or doors of the factory are left open. An excess of silica must always be taken, to make up for that which volatilizes. This excess must be materially increased when the higher-grade alloys are to be prepared. Since this volatilization of silica requires power, it follows that it takes more power in proportion to make a high-grade than to make a low-grade silicide. We use about twice as much power to make an alloy of thirty-five per cent. as to make one of twenty-five to twenty-seven per cent. The silicon in the former alloy is correspondingly more expensive.

USES.

On account of their great purity and small bulk these silicides are superior to those made in the blast-furnace, but they can only be used instead, where the character of the work admits of paying a larger price for the unit of silicon.

These alloys are very resistant against acid oxidizing agents and conduct electricity well. They are a cheap material for anodes for electrolysis in aqueous baths. The lower grades make nice correct castings. We exhibited, in Atlanta, in 1895,

some articles cast from a twenty-five per cent. alloy. These low-grade alloys can be used for making luxury articles, statuettes, etc. The metal when polished has a beautiful, and lasting luster. The higher grades and also the lower grades may perhaps be used instead of aluminum in the heating process of Goldschmidt. This process consists of mixing aluminum foil with some substance capable of yielding oxygen, and igniting the mixture at one point. The reaction between the aluminum and the oxygen, if started at one point, gradually proceeds through the whole mass and a heat is produced, which, in intensity, is second only to that of the electric arc. The silicon of the iron silicide may replace the aluminum, and can be made for a lower figure. These silicides are valuable abrasives, being very hard, and still easily crushed.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY
OF MICHIGAN.]

PERHALIDES OF QUINOLINE.¹

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THE most of the work reported in this paper was completed in the spring of 1897. Publication was delayed because the author hoped soon to be able to complete the study of the halogen salts of quinoline, and the action of the halogens upon these salts and upon the base itself. Other duties have prevented this until it is deemed advisable to present the work in so far as ready, hoping to continue the research during the following year.

The halogen salts of quinoline have been known for a long time, yet only the chloride² seems to have been reported. No attempt was made to prepare this salt in crystalline form. For the experiments where the chloride was used it was assumed that it was formed by the addition of an excess of hydrochloric acid to the base. The results confirm this assumption.

An attempt was made to prepare the quinoline hydrobromide in pure condition. A mixture of the acid and base was warmed

¹ Continuation of previous paper. This JOURNAL, 19, 553.

² Schiff: *Ann. Chem.* (Liebig), 131, 112.