SESSION V

April 26, 1989

<u>Chairmen:</u> A.C. Sims, The Ferroalloys Association - USA.
D. Ksinsik, The Ferroalloys Association - Canada.

<u>Introductory Address:</u>
"The Direct Synthesis of Methyl Chlorosilanes: Silicon and Trace Elements", A. Ritzer, General Electric Company - USA.

*1. **"Characterization of Silicon Metal"**, K.S. Chopra, Elkem Metals Company - USA.

*2. **"Roasted Wood: A New Raw Material for Silicon Metal Production"**, M. Dubrous, Pechiney Electrometallurgie - France.

*3. **"Development and Use of Silgro Carbon-Silica Briquettes in Silicon\ Metal Furnaces"**, G.W. Lask, AIMCOR - USA and N. Ruuth, KemaNord - Sweden.

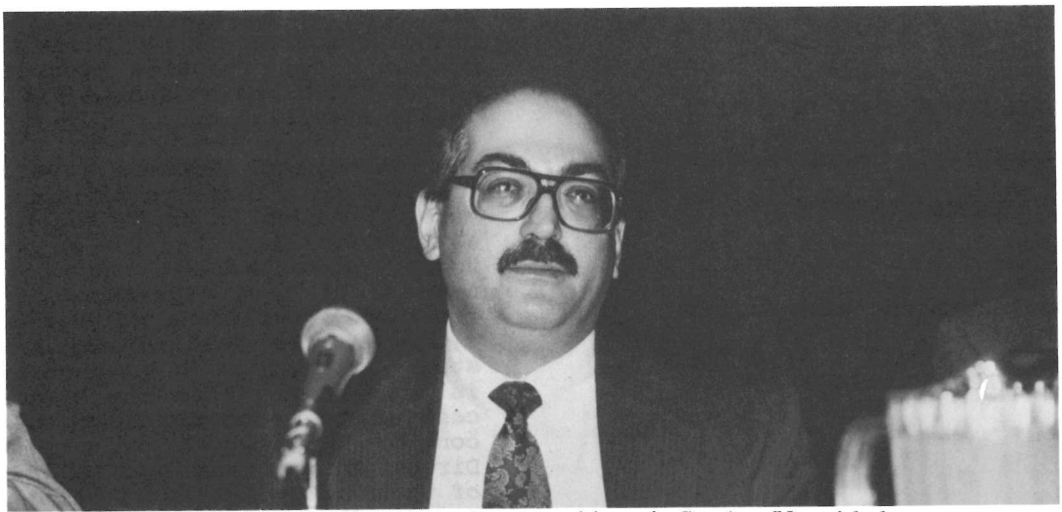
*4. **"The Several Utilizations of Slag from Ferro-Alloy Manufacture"**, Y. Yamamuro, Pacific Metals Company, Ltd. - Japan.

*5. **"The Application of Quality Assurance in the Production of Ferro Boron Using S.P.C."**, J. Pearson, London & Scandinavian Metallurgical Company, Ltd. - United Kingdom.

*6. **"Expert Systems Can Control Ferroalloy Production Processes"**, T.K. Leonard, Elkem Metals Company - USA.

*7. **"Occupational Health Aspects of Risk Management in Elkem Metals Company"**, C.R. Allenbach/ W.R. Pioli, Elkem Metals Company - USA and J.P. Lutzow Holm, Elkem - Norway.

*These papers can be found in Volume I of the Proceedings



A. Ritzer of General Electric gave introductory address in Session V entitled, "The Direct Synthesis of Methyl Chlorosilanes: Silicon and Trace Elements.

A.C. Sims and Vice Chairman D. Ksinsik with first-half speakers K.S. Chopra, M. Dubrous, G.W. Lask, and N. Ruuth.

The second half of Session V featured speakers Y. Yamamuro, J. Pearson, T.K. Leonard, C.R. Allenbach, and W.R Pioli.

THE DIRECT SYNTHESIS OF METHYL CHLOROSILANES: SILICON AND TRACE ELEMENTS

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Current sales of silicon to silicone producers is approximately 400 million pounds/year, and should grow at a rate of more than 10% per year for the foreseeable future(1). While the silicones industry is not the largest segment of the silicon market, it may be the fastest growing. The reasons for this stem from the fact that the silicones industry is young, having been started in the years just after World War II. This means that many markets now served by silicones are not fully penetrated. It also means that new uses for existing silicone polymers are constantly being developed. Finally, new silicone polymers are being synthesized, some of which will be commercialized. The economic future for silicone producers is bright, which means silicones are an attractive market for silicon producers.

Silicon and methyl chloride are the raw materials for the entire silicones industry. That this is true is due to the discovery of the "Direct Process" in 1939 by Eugene Rochow. The Direct Process is

$$Si + 2CH_3Cl \text{ -----> }$$

$$\begin{array}{ccccc} & & Cl & & \\ & & | & & \\ CH_3 & --- & Si & --- & CH_3 \\ & & | & & \\ & & Cl & & \end{array} + \text{by-products}$$

Rochow's great discovery was copper catalysis. The reactants are inert without it. In the presence of copper and other important trace elements, the reaction proceeds and the main product is dimethyldichlorosilane (Di). Today the reaction is carried out continuously in fluidized bed reactors at approximately 300°C. Methyl chloride gas fluidizes silicon powder. The reaction products are vapors which are condensed and purified by distillation.

The Direct Process remains the only economic route to silicone polymers. Without it there would not be a silicones industry as we know it today. Nevertheless, the production cost of Di is a significant part of the cost of silicone polymer production, and the cost of silicon is a stand-out cost in Di production. It is fair to say that the Direct Process is the economic heart of silicone production. For this reason the Direct Process has been the subject of thousands of papers in the literature. Much of this work has been directed to identifying the critical variables that control rate and product distribution, and the goal of most workers has been to maximize the yield of Di in order to minimize the consumption of silicon. There is general agreement that copper is required to make the reaction proceed. Beyond this there is confusion and contradiction. Virtually the whole periodic table has been added to Direct Process reactors but there is little agreement on the results - a shocking state of affairs in view of the significance of the Direct Process to the economics of the entire silicones industry.

It may appear to silicon producers that an inefficient Direct Process is to their advantage, since it requires more silicon to produce the required amount of Di. Of course in the long run this is not so. Efficiency in silicones production leads to lower costs to customers, expanded markets for silicones, and better profitability for silicone producers, all of which ultimately will benefit silicon producers.

In the following we summarize our work on trace elements that led us to a catalyst formulation that gave a marked improvement in Di yield. We hope this work may suggest how silicon producers may improve their product in ways that will reduce costs for silicone producers.

Running the Direct Process can be considered both art and science. So many variables affect rate and product distribution that it requires extraordinary care and control to carry out the reaction reproducibly, and in such a manner that the results will be relevant to industrial scale production. Thus our first job was to construct reactors in which all the important reaction parameters were known and controllable. Since we have previously published our work [2], only a summary of it is presented here.

Our work extended over six years and involved hundreds of laboratory runs. The same batch of silicon powder was used throughout. The silicon used was "chemical" grade and contained the elements listed in Table IA. Silicon pieces centimeters in size were ball milled, separated into various size fractions by aerodynamic/centrifugal classification and then blended to obtain a mixture having a surface area of $0.5 m^2/gm$. The size distribution is listed in Table 1B. The copper, zinc, tin, and methyl chloride used were highly purified.[1] Two types of reactors, fluidized bed and stirred bed, were used. The reason for using both types was that it was not known if reactor type was an important variable. As it turned out, the reactors gave identical results within the scatter of the data. Maintaining a uniform temperature in the reactor is essential for reproducibility, and in the case of the fluidized bed reactor, good fluidization was essential. The latter was assured by being able to see the silicon at all times during the reaction. Details of the reactor design that made this possible have been described[2] in sufficient detail that others could duplicate them.

The principal results of our work were that (1) minute quantities of tin have a profound impact on rate and product distribution (a fact that was missed in all published work prior to ours) and (2) that tin and zinc have a synergistic effect. Table II presents results for a series of runs to evaluate the presence or complete absence of copper, zinc, and tin. The interested reader can follow through the results in detail. The key points are: (1) The reaction does not proceed in the absence of copper, as expected, and (2) copper, zinc, and tin together result in extraordinary selectivity for Di, and high rate. The performance shown in Run E, Table II is significantly superior to any published previously and is highly significant from an economic standpoint.

Many experiments were done to determine the effects of the absolute and relative amounts of copper, zinc, and tin, as well as temperature. Complete results have been reported.[2] Perhaps of most significance is that over a wide range of tin to copper ratios, product distribution was constant, but reaction rate was a strong function of the amount of tin present. However, beyond a tin to copper ratio of approximately 0.0025, the residue (primarily methylchlorodisilanes) content of the product increased drastically. We believe the critical variable to be the tin to copper ratio, not the absolute tin concentration in the bed. Other results were that there is an optimum although broad range of zinc to copper to maximize selectivity, rate was almost independent of zinc concentration, temperature between 300^{o} and 320^{o}C had little effect on selectivity, and copper had an effect on rate but not selectivity.

We believe our work represents a significant improvement in the practice of the Direct Process. We have shown how to construct and operate laboratory scale reactors and how to analyze reaction products so that reproducible and meaningful results can be obtained. Despite this, there is yet much to learn about the Direct Process and silicon producers are in a position to contribute substantially. There is a consensus that aluminum is a necessary ingredient of silicon for an effective Direct Process. The effect of other trace elements such as iron, magnesium, titanium, and calcium is ambiguous. It is reasonable to suppose at least some of these elements are important. The question of their importance is enormously complicated by the fact that their effects are probably dependent upon the levels and chemical state at which they are present, and the grain size of the silicon. An advantage can be derived by the silicon producer which produces the most effective silicon for the Direct Process. One may even imagine the time when all the needed ingredients, including copper, zinc and tin, are present in the silicon sold to the silicone producer. Cooperative efforts between silicon and silicone producers may be the key to achieving the optimal Direct Process.

References:

1. "The Chemistry and Technology of Silicones: Part I Production of Starting Materials", Schliebs, R., Ackerman, J., Chemie in Unserer Zeit, 21, No. 4 (1987).

2. "Catalysis of the Rochow Direct Process", W. J. Ward, A. Ritzer, K. Carroll, J. Flock, J. Catal., 100, 240 (1986).

TABLE I

A. Trace Elements in Silicon

Element	Amount (ppm)
Iron	5600
Aluminum	2700
Titanium	850
Manganese	200
Calcium	160
Nickel	120

B. Silicon Size Distribution

Weight %	Particle size (µm)		
	Maximum	Minimum	Midsize
25	25.4	1.3	9.8
19	81	12.7	39
37	64	16	43
11	203	32	92
8	521	124	256

TABLE II

Effects of Copper, Tin, and Zinc on Rate and Product Distribution*

Run	%Cu	%Zn	%Sn	Rate (K)	T/D	MH	Mono	Residue
A	0	0.5	0.005	0	--	--	--	--
B	5	0	0	13	0.21	3.7	8.8	1.9
C	5	0.5	0	16	0.09	2.0	3.0	1.9
D	5	0	0.005	46	0.12	1.0	7.2	2.2
E	5	0.5	0.005	84	0.05	0.4	2.4	1.3

SESSION V - DISCUSSION

"THE DIRECT SYNTHESIS OF METHYL CHLOROSILANES: SILICON AND TRACE ELEMENTS"

Q. A.C. Sims, Globe Metallurgical, Inc. - USA. What advice can you give the producers of silicon metal with regard to how they can improve their product for the manufacturing of silicones?

A. A. Ritzer, General Electric Company - USA. I think more rigorous control using perhaps more sophisticated analytical techniques on a routine basis, as well as using that data for SPC purposes and understanding of the consistency of process in the regards that are important to us.

Q. W. Shen, Union Carbide Corporation - USA. You commented on the high purity silicon giving you a low reaction rate. Could you comment on the impurities in silicon, for instance Fe and Al, what is the catalytic effects of these elements, are there upper limits for these impurities in the silicon?

A. A. Ritzer. We routinely specify levels of aluminum, iron and other trace elements, and often use a window to get the effective results we need. Aluminum is definitely required as an in situ promoter. Hyper pure silicon does not work.

Q. J.A. Kruger, Silicon Smelters Samancor - South Africa. Can you please comment on what roll calcium disilicide places in your process?

A. A. Ritzer, General Electric. At General Electric we have the perception and evidence over the years that excessive calcium disilicide can lead to difficulty from a safety viewpoint in grinding material; as such, we have a test for that purpose.

"CHARACTERIZATION OF SILICON METAL"

Q. S. Argyropoulos, University of Toronto - Canada. Is it possible to measure intermetallic formation during the actual process with these techniques? In other words, to see the kinetics of that formation?

A. K.S. Chopra, Elkem Metals Company - USA. I think it is possible, but the melting point of silicon is very high. There are techniques available in scanning electron microscopy where you can heat a sample up to 1000°C and observe in situ as it is heated. Anything over that temperature would be very difficult to do.

Q. A.C. Sims. Of the various tools that you have described in this paper, is it possible to select the most useful tool and to explain why it is the most useful tool?

A. K.S. Chopra. Generally, most people have access to a scanning electron microscope. For example, you can look at the polished as well as the fractured surface. You can do a certain amount of work using this tool and get good information, because the state of the art has improved to the point where they can do the light elements. Carbon, oxygen and nitrogen can be determined using a scanning microscope interfaced with an EDS system. If you want to determine the valence state, binding energy or the kinetics of reaction, which the previous speaker has already demonstrated very well, you need Auger or ESCA. If you cannot afford to have those you can go out and get that service. The most important tool at this point, in my opinion, is to have an x-ray energy interfaced with scanning electron microscope, which is capable of doing light elements.

Q. O. Raaness, SINTEF - Norway. It was said using silicon for chlorosilanes is absolutely necessary to have aluminum in the silicon, and he also said something that active spots could be found where there is no oxide layer. You said a lot more oxides in the aluminum silicides. Do you have any comments on that?

A. K.S. Chopra. I did microprobe analysis and electron microscopy on the field. If you let the sample sit around for days or months, you will develop more of an oxide film on the aluminum containing phase and in general the silicide phase itself. In addition when I did the probe analysis, the oxygen was still not detectible. In other words, it was still parts per million. It is strictly a surface phenomena rather than oxygen in the silicide phase itself.

A. Ritzer, General Electric. In the commercial practice of chlorosilane synthesis we use high energy guns to generate a lot of fracture surface in situ such that the native oxide layer does not play a part in the on-going continuous reaction.

"ROASTED WOOD: A NEW RAW MATERIAL FOR SILICON METAL PRODUCTION"

Q. J. Pearson, London & Scandinavian Metallurgical Co., Ltd. - UK. Could you tell me please, if you have a laboratory test to measure the reactivity of the roasted wood?

A. M. Dubrous, Pechiney Electrometallurgie - France. Yes, we have a test laboratory for the measurement of activity of carbonaceous products. We made different tests for physical reactivity and chemical reactivity. For roasted wood, we found that reactivity as good as charcoal and a little better than wood chips.

Q. O. Raaness. This is a very dry material, and do you never experience the problem of self-ignition in this material?

A. M. Dubrous. We have no problem of ignition of roasted wood because out of the roaster it is wetted at the level of 6%. This avoids dust in handling and prevents all self-ignition of the product. During three years no problems of self-ignition have occurred with roasted wood.

"DEVELOPMENT AND USE OF SILGRO CARBON-SILICA BRIQUETTES IN SILICON METAL FURNACES"

Q. E.K. Stanley, AMTC - USA. You said you changed the spacing of your electrodes and you changed the electrical parameters. Could you tell us in which direction you changed the spacing and by how much?

A. N. Ruuth, KemaNord - Sweden. We went inward towards the center about 150 to 200 millimeters. We went up with the voltage and down with the current.

Q. A. Arnesen. You referred to the fact that with briquettes, some days with major mechanical problems had been eliminated from the numbers. In your reference material for the normal before briquettes, did you eliminate in the same way?

A. N. Ruuth. Yes.

"THE SEVERAL UTILIZATIONS OF SLAG FROM FERRO-ALLOY MANUFACTURE"

Q. H.S. Aswath, Maharashtra Elektrosmelt - India. What is Mn content in FeMn slag?

A. Y. Yamamuro, Pacific Metals Company, Ltd. - Japan. About 10%.

H.S. Aswath. (Comment). In Maharashtra Elektrosmelt we are converting the FeMn slag into granulated slag. The granulated slag is cleaned then used in an integrated iron and steel plant. Since it is a granulated slag we pass it through the sintering plant, sinter it along with the iron ore fines, convert it into sinter and use it in the blast furnaces. The advantage was that in the sintering plant this granulated slag helps to improve the permeability of the charge and thereby increase the productivity of the sintering machines. It also enables the use of the sinter, which has a high manganese content, and manganese is useful in the blast furnace for increasing the Mn content, for improving the performance of the blast furnaces with regard to the desulfurization of the slags and also to improve the rate of driving of the blast furnaces.

Q. R. Buscamante, Cerro Matoso S.A. - Colombia. What was the iron content of the nickel slag?

A. Y. Yamamuro. About 4%.

Q. D. Ksinsik, SKW Canada Inc. - Canada. Could you indicate to us the extent of slag conversion you experienced in your plant, what percentage of slag your generated could you convert into other products?

A. Y. Yamamuro. About 25%, and fiber about 1.5%.

"THE APPLICATION OF QUALITY ASSURANCE IN THE PRODUCTION OF FERRO BORON USING S.P.C."

Q. D. Ksinsik. Could you evaluate what percentage of your total effort you have undertaken to obtain quality assurance was concentrated on S.P.C.?

A. J. Pearson. Quite a substantial amount. It is still ongoing. We are applying it to all aspects of production which we think are important. I would say somewhere between 25% and 50%.

Q. R.F. Silver, Elkem Metals Company - USA. Thank you for effectively highlighting the direct connection between quality assurance and cost benefits. However, I find it interesting that you did not discuss the tremendous impact that the price of its major ingredient, boric acid, has on the product. Can we really reach so far with quality assurance that we can overcome the impact of something that contributes to maybe up to 65% of the cost of the product?

A. J. Pearson. You are quite right that the boron raw material is a very significant fact, and I think that quality assurance can optimize that. But it is very difficult for us to go any further because we are in the hands of the boric acid producers. There are alternative raw materials, where the boron units are cheaper if one can utilize them.

R.F. Silver. (Comment). We are in the hands of the supplier of the major ingredient of the product. After many years of usage of charcoal we have a pretty effective quality standard which our charcoal suppliers meet. However, we still face the problem that amorphous alloys have not succeeded, not for some of the reasons implied, but rather because of the price of its major ingredient.

J. Pearson. (Comment). I think that is the story that amorphous producers put about. I think there is much more to it than that. They have tried to introduce a technology which is meeting resistance from their customers for a number of reasons, including the lower energy costs and the problems of manufacturing a new type of transformer. I think they blame us, but I don't entirely go along with it. They knew the numbers before they started.

R. Buscamante.(Comment). We have been working with S.P.C. techniques since 1986, and really it is a good tool for quality assurance. I have an observation related to the position of Mr. Pearson, on the occasion which they have a batch of ferro boron out of specification because of charcoal. Probably one of the most important things in this quality assurance philosophy is the control that the supplier must do on the raw materials given us. Our experience has been that as the suppliers are acquainted with the S.P.C., they are increasing the quality of the raw materials and it is the way to avoid the batches out of specification.

J. Pearson. (Comment). I very much agree with your comments. I was showing that as an example of something that had gone wrong before we fully understood all aspects of the charcoal, and we use that as an example to have further discussions with our suppliers and try to educate them more in these techniques.

"EXPERT SYSTEMS CAN CONTROL FERROALLOY PRODUCTION PROCESSES"

Q. D. Ksinsik. Are we, the human experts, the engineers able and capable, or will we become able and capable, to describe precisely the problem cost cases, with all the necessary process variables which sometimes we don't even have?

A. T.K. Leonard, Elkem Metals Company - USA. It is a difficult process in getting the expert, in this particular case the production engineer, to verbalize what he knows. He knows it so well now, because he has been doing it so long, that he can in many cases evaluate the indicators on the furnace without going through a conscious process. It almost subconsciously comes to him. Because of that he has a difficult time describing it so that I can put it into the knowledge base. But the give and take process goes on and we do then get sufficient evidence, sufficient facts and rules of thumb or rules of judgment to put into the knowledge base. I don't suppose there is a perfect metallurgical engineer or a perfect expert, so there will always be something more to be added to the knowledge base. It will never be complete, but there is expertise out there and we need to capture it in such a way that it can be preserved and used by other people.

Q. S. Argyropoulos. Do you have some real time expectations from your expert system?

A. T.K. Leonard. Yes. Real time in the case of mix systems specials is on the order of hours. The user will not go to the system on a minute-by-minute basis. He will go to it two or three times a shift.

Q. S. Argyropoulos. What sort of hardware are you using?

A. T.K. Leonard. The particular hardware that we are using is a Texas Instrument Explorer System.

Q. S. Argyropoulos. Is the interface between your process control computer and this computer serially or is that through a RS232?

A. T.K. Leonard. RS232 over X modem. It is not particularly fast, but it is adequate.

Q. D. Ksinsik. The system that you have described is quite complex. Given the different structure of our industry regarding company sizes, what would you see as the minimum threshold expense for application of the system in companies?

A. T.K. Leonard. With the advent of the 386 processor in IBM PCs or their clones, $5,000 will get you a pretty good piece of hardware, and another $5,000 will get you a shell that you can work with. It might not be the shell that you finally want to use, but will enable you to explore and to go at least part of the way to building a usable expert system. So it is a minimal risk.

Q. D. Ksinsik. And what about software? Would you eventually look to commercialization of the software you are developing?

A. T.K. Leonard. We are using a commercial shell at this point that is available to everyone. The knowledge base itself is proprietary. The information in the base is proprietary.

D. Ksinsik. (Comment). The fact that Mr. Argyropoulos has intervened quite heavily, shall give us an opportunity to send out the message. We do not forget that we try to imitate human expert knowledge. That means that we still need creativity and the message will be pleased to provide creativity with well trained, well educated young engineers. We need them, really, in our industry to have success in the future.

T.K. Leonard. (Comment). An expert system does not replace humans. It simply assists them. It allows them to raise their sights and think of more difficult problems.

"OCCUPATIONAL HEALTH ASPECTS OF RISK MANAGEMENT IN ELKEM METALS COMPANY"

Q. J. Kruger, Samancor - South Africa. My question is about amorphous silica. Is there any distinction between the crystal of amorphous silica as far as the exposure levels, exposure level multipliers and health effects that you can expect from it? What work is done in that regard to distinguish between the two?

A. C.R. Allenbach, Elkem Metals Company - USA. The international agency for research on cancer, and other organizations, within the last year have looked at both amorphous and crystalline silica.

On the basis of reasonably good information, they have, deemed amorphous silica not to be a cancer causing material. In the case of crystalline silica, which can be disputed, and we as an industry have never experienced a cancer development from exposure to crystalline silica, these agencies have deemed it a carcinogen on the basis of animal tests, not on human tests. Now the consequence of that problem is that in the United States we have a rule or a law called "The Hazardous Chemicals Rule." And that rule has a portion in it that states that when one of those agencies, deems a material a cancer causing agent, it is deemed that way. Then you have to treat it and forever try to face up to minimizing risks of exposure. Many organizations in the country are arguing about the designation of crystalline silica. The other part of your question, I think, was, "Are there differences in the standards? Yes. The exposure standard for amorphous silica is considerably higher, than for crystalline silica.

Q. D. Ksinsik. Can you share with us your view of what the future has in store with regard to the subject of health management?

A. C.R. Allenbach. I think all three of us could answer in a couple of words. It is going to get a lot more stringent, a lot tighter and give us a lot more work. The reason I say that is that the public is learning more and more about this from rules like in the United States the Hazard Chemicals Rule. Analytical procedures are getting better all the time, and as they find smaller and smaller amounts, the environmental people will want to regulate you down to the smaller and smaller amounts. Along with that the legal profession, especially in the United States, has developed a very strong group that is very well up on environmental rules and the work-place rules, and with the public being more and more concerned, the litigious end has found a very good place to work on those financial risks. So overall things will progressively get a little tougher.