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THE ELECTROLYTIC
PREPARATION OF THE ALKALINE EARTH METALS.

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• of the University of Minnesota by Walter
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THE ELECTROLYTIC PREPARATION OF THE ALKALINE EARTH METALS.

The first experimenter to obtain one of the alkaline earth metals was Davy, who, in 1808, electrolysed calcium chloride with a mercury cathode and distilled the resulting amalgam. Since his day, but more particularly in the last fifteen or twenty years, three general methods have been worked out.

I. Reduction of the oxide or chloride with a stronger metal,

II. Electrolysis of a solution, generally of the chloride, with a mercury cathode, followed by distillation of the amalgam, and

III. Electrolysis of a fused salt.

Of these three, in the case of calcium the third has been the most successful; in fact the metal is prepared on the commercial scale by this process. In the case of strontium and barium, only the first two have yielded any results. Some have obtained a few small shots of metallic strontium by the third method, and

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Willner^U in one experiment obtained a lump of 1.2 grams but was unable to repeat the performance. Barium has never been so obtained. It is perhaps worthy of notice that numerous patents have been issued for the preparation of all three metals by electrolysis of the fused salts.

The present investigation was undertaken with the purpose of preparing strontium and barium by direct electrolysis. Preliminary experiments showed so many difficulties that the preparation of calcium was taken up for the sake of experience. In this connection certain details were worked out, a crucible for the electrolysis of fused salts designed, and the "Anode Effect" studied. This work took so much time that practically nothing was done on strontium and barium.

THE PREPARATION OF CALCIUM.

There are two general forms of the apparatus for

- (1). Kurt Willner, - Dissertation, Berlin, 1907.

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the preparation of calcium. In that of Borchers & St~~ockem~~⁽¹⁾ a ring of carbon blocks is the anode, and an iron spike set in a water-cooled brass collar in the bottom of the furnace, the cathode. The calcium collects as a sponge, and is spooned out and squeezed to free it from adhering chloride. The other, which is the one used commercially at Bitterfeld, has been described by Goodwin⁽²⁾ and modified by Tucker and Whitney.⁽³⁾ It consists of a graphite crucible used as anode, and a water-cooled iron cathode so arranged that it can be raised as the calcium collects, thus withdrawing a continuous stick of the metal.

A 4"X4" graphite block, 5" long, was used for a crucible. A hole 3" deep and 3" in diameter was turned in one end, and another, $\frac{1}{2}$ " deep and somewhat larger, in the other end, to receive a cooling coil of lead pipe. This coil was to freeze a layer of electrolyte on the

(1). Borchers, Electrometallurgy, p.

(2). J. Am. Chem. Soc., XXVII. (1905). 1403.

(3). J. Am. Chem. Soc., XXVIII. (1906). 84.

4.

bottom of the crucible, thus causing the electrolysis to go to the sides with consequent evolution of chlorine there rather than directly under the stick of metal. An anode was constructed of $\frac{1}{2}$ " gaspipe. The crucible was placed on a large block of graphite, which carried a lug to which the cable could be attached. Connection to the crucible was made simply by contact of the graphite surfaces.

At the start, the crucible was placed in a resistance furnace and a charge of granulated calcium chloride melted down. It was then removed and placed in position for electrolysis. In succeeding runs, the current was started by fusing a channel in the surface of the electrolyte by means of a blast lamp, after which the whole charge melted quickly. After one or two attempts, it was found to be quite easy to obtain satisfactory electrolysis, giving coherent sticks of calcium about $\frac{1}{4}$ " in diameter. The question of additions to the bath during electrolysis came up. Tucker and Whitney fused

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calcium chloride over a blast and added it while liquid. They mention this as being necessary to free it from water. It was found, however, that three or four minutes heating in an iron crucible over a four-post burner gave a product that could be added during electrolysis and would melt quietly. Several runs were made in this apparatus, the average current being 75 amperes at 25 volts. No exact figures on which efficiency could be calculated were kept, tho from later experience, it would seem that the quiet electrolysis and regular sticks of metal pointed to a very high efficiency. During these runs the anode effect appeared periodically with remarkable regularity, in one case occurring exactly once a minute for some twelve or fifteen minutes without a break.

It now became evident that a modification of the apparatus would be desirable. The crucible was nearly eaten thru, being only about $1/16"$ thick in places. The connections were highly unsatisfactory, every movement of the crucible producing arcs which more than once melted thru the lead coil, and wire wound round the crucible also

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failed, as, due to the square corners, contact was poor and local and the wire soon burned out. It was also thought that a larger crucible might prove more efficient, due to greater distance between the chlorine evolved and the stick. Further, the anode had been closed with an ordinary cap, which burned thru, allowing the cooling water to come in contact with the bath, which caused violent explosions, throwing the molten chloride about. Accordingly a new anode was made of $\frac{3}{4}$ " iron pipe, closed with a plug at least 1" long, and ^{the} cooling water entering thru 3/8" lead pipe extending to within 1/4" of the plug. A new crucible was turned from 5" round graphite, with a cavity $3\frac{1}{4}'' \times 3''$. Connection was made by bolting a band of heavy sheet copper around the crucible, the cable being attached to a lug formed by the projecting ends of the bands. The apparatus was then set up as in Fig. 1., and so used in all future runs, except for the packing shown around the top of the crucible. The electrode feed of an arc furnace was used, and the whole set up in a wind furnace, the arc furnace being outside on the

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edge, and the crucible resting on bricks placed on the grate bars. It was planned to investigate the following details:-

- I. Determine the efficiency and compare it with efficiency of the Borchers' furnace,
- II. Investigate the effect of purity and temperature of electrolyte on the yield,
- III. Study the anode effect,
- IV. Find some method of melting or casting metallic calcium.

E F F I C I E N C Y.

Goodwin obtained an efficiency of 26.6%. Tucker and Whitney introduced the water-cooled ^{cathode} anode for the purpose of increasing this, but give no figures. Woehler["] obtained an efficiency of 80% in a different apparatus. In the present investigation it was early noticed that at times the electrolyte was very viscous and pasty, and that at these times a very poor electrolysis was obtained. The metal was branched and uneven, and enclosed large

(1). Zeitschr. Elect. XI. (1905), 612.

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lumps of chloride and carbide. From one such run, the metal obtained (after being cleaned by dissolving off the adhering chloride with absolute alcohol) weighed 21 grams. The electrolysis lasted 1 hour and 20 minutes at a current of 80-100 amperes at 28 volts. The total ampere-hours, calculated from five-minute readings, was 100.4, the total power 2.66 kilowatt-hours. This is equivalent to an ampere-efficiency of 28.1% at a cost of 126.6 watt-hours per gram.

It is agreed by all who have worked on the problem, that the temperature should be kept as low as possible. In one run, under fair conditions, except that the temperature was kept uniformly high, the following figures were obtained:-

Average amperes - 175-180	Total ampere-hours,	305.0
" volts, 17 - 20	Kilowatt-hours,	6.216
Time, 1 hr. 45 min.	Yield-grams,	107

Ampere - efficiency - 46% 58.1 watt-hours per gram.

The arrangement of the furnace room was such that it was impossible for one person to conduct an electrolysis and take readings if the furnace required any at-

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tention. So no other complete runs were recorded as no figures were obtained from the Borchers' furnace, tho in many runs an efficiency much higher than either of the above was certainly obtained, as in the above the conditions were purposely kept very unfavorable.

It was desired to investigate the Borchers' furnace, as nothing has been published giving its efficiency. A similar furnace was available, and it was remodelled to conform to Borchers' design as shown in Fig. 2. A ring of graphite blocks were set in place, a mixture of sand and waterglass stamped in, and the cracks between the blocks filled with a mixture of molasses and graphite dust. In four equidistant places, strips of heavy copper were driven between the graphite blocks, and connected by heavy wires to the positive cable. The graphite cap, as shown, was replaced by an iron cone about 50 mm high. A floor of fluorspar was stamped in, and then a charge of calcium chloride melted down by placing a small carbon rod across the furnace, touching the cathode. No results were obtained. The maximum current available,-250

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amperes, - failed to keep even apart of the bath fluid; some calcium separated out on the cathode and rapidly grew across to the anode, shortcircuiting the furnace, and then the whole quickly froze up. All attempts to open it up were unavailing, so this work was abandoned.

Attempts were also made to prepare alloys in this furnace with some success. The copper strips were removed, the iron cone replaced by a carbon electrode as shown, and a bottom of graphite dust and molasses stamped in and baked with the arc. This whole crucible was used as cathode, a carbon rod suspended from an independent stand being the anode. Some calcium chloride was fused in, and electrolysis begun. The anode affect was permanent, causing a drop across the furnace of about 80 volts, so that the power, with a current of 60-70 amperes, was sufficient to keep the bath fluid. Lead was now added, and after about an hour, the melt was tapped into an iron mould. The resulting alloy, on being struck with a hammer while hot, crumbled into a mass of silver-white crystals, tarnishing only after considerable time.

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As no pyrometer to study them with was available, the preparation of alloys was also abandoned.

EFFECT OF COMPOSITION OF ELECTROLYTE.

All the way thru the work, it was noticed at various times, that the electrolyte would sometimes fail to act properly, becoming viscous and infusible, the liberated chlorine carrying it up in great bubbles to form a froth which solidified over the top of the crucible, stopping the run. After giving up work on the B^orchers' furnace, the Goodwin furnace was again taken up, and a run started with material taken out of the old Borchers' furnace.

Alternating current was now available, and it was thought to melt down a charge with it and then change over to direct current. The melt behaved very badly, 350 amperes giving a melt only partly fluid. 450 amperes, at a bright white heat, gave a perfectly fluid melt, but on throwing on direct current, (250 amperes) it rapidly froze up. Samples were taken from the semi-fluid melt, and then it was scooped out and replaced by fresh calcium chloride as far as possible without interrupting the cur-

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rent. The bath now opened up and fairly satisfactory electrolysis took place, tho the stick was badly branched and could be seen to burn at the edges. This was the run mentioned before as having an efficiency of 46%. No satisfactory runs were ever obtained with a current as high as this, 80 - 100 amperes giving about the proper temperature.

It seemed as tho the age of the electrolyte was responsible for its viscosity. Woehler⁽¹⁾ is the only one who has mentioned this, and he lays it to the formation of the hydrated oxychloride. This seemed improbable, and it was thought that the infusibility might be due to the presence of oxide, from shots of metal falling from the stick, the stick burning, etc. Arndt⁽²⁾ finds 7.5 parts of Ca O to be soluble in 100 parts Ca Cl₂, at this temperature, but this should lower the melting point. Analyses were made on the electrolyte from the two parts of the above run, taking about 5 grams for each, with the fol-

(1) Loc. Cit.

(2) K. Arndt. Berichte, XL (1907), 427.

13.

lowing results:

	Free Carbon	Alkalinity as Ca O	Fe ₂ O ₃
Pasty Electrolyte	1.60%	4.40%	-----
	1.15	4.05	0.05%
	1.09	----	0.08
Good Electrolyte	None	0.420	0.048
	None	0.426	0.052
Fresh calcium chloride	None	0.03	trace
	None	0.03	trace

Two samples from the first runs where this was noticed, one of a poor electrolyte and one a good electrolyte, gave 3.58% and 0.15% Ca O respectively. The alkalinity is very evidently to blame, but this is much less than Arndt finds to be soluble. I have no explanation to offer for the deficiency.

THE ANODE EFFECT.

In the first few runs it was noticed that at times the voltage across the bath would suddenly jump from 15-25 to 65-70; with a corresponding drop in current, remain so for a few seconds and then as suddenly drop back to its normal value. At these times it could be seen

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that the chlorine, instead of bubbling up in the ordinary manner, formed a continuous sheet, so that the electrolyte did not make contact with the crucible, and the current passed by a multitude of tiny arcs. It was always accompanied by a hissing sound, and the pointers of the switch-board instruments vibrated over a range of 5-10 divisions so that readings of voltage and current were only approximations. Readings from such a run, taken every 30 seconds, during the effect, are plotted in Fig. 3. "Drawn" means that at that point the stick was raised; "Ca Cl," that additions were made to the bath.

There are not many mentions of this in the literature, but Willner gives a very full discussion. Willner used a porcelain crucible, and an iron rod for cathode and carbon rod for anode. He says:- "Soon after beginning the electrolysis the disturbances appear. The drop across the bath rises from its normal value of about 8 volts with 25 amperes to about 40-60 volts, and the current drops correspondingly. Around the anode a blue light appears, the evolution of chlorine ceases, and there is a

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chattering noise. These disturbances often disappear spontaneously, but occassionally they cause such strong currents in the melt, due to the rise in temperature at the anode, that the electrolysis must be stopped. I only observed this occassionally with calcium chloride, but with strontium and barium chloride it occured regularly." He further says that moving or drawing out the cathode has

no effect, that putting in a new carbon anode restored normal conditions, as did also moving the anode. He says that touching the ^{anode} neade with an iron wire restores the current to its normal value, showing that the disturbance is caused by a skin of some sort on the anode. He then quotes Lorenz,⁽¹⁾ Borchers,⁽²⁾ Muthmann,⁽³⁾ and Woehler.⁽⁴⁾ Lorenz describes the effect as appearing like the Wehnelt interrupter, and explains it as being a "polarisation

(1) R. Lorenz, Zeitschr. Anorg. Chem., XIX (1899), 246.

(2) Borchers, "Electrische Ofen", pp. 13-14. (1907).

(3) Muthmann, Liebig's Annalen, 320 (1901), 249.

(4) P. Woehler, Zeitschr. Phys. Chem. XXXIV (1900) 529.

phenomenon like the aluminum electrode."

Borchers, discussing the electrolysis of cryolite holds that the high anode current density is responsible, and says:- "The quantity and pressure of the gas evolved on the relatively small anode surface cause the formation of an almost uninterrupted layer of gas, which the current can only pass by forming a number of very small arcs. The result of this is an especially strong heating of the coating of the anode. This increases the pressure of the gas, and the size of the layer, with consequent increase in the voltage."

Muthmann says that the decreased evolution of chlorine is due to combination of the gases with the carbon of the electrode. Lorenz simply mentions it and does not attempt to explain it.

Willner then discusses the above explanations and rejects them all. He claims it to be due to silica, forming an insulating skin on the anode. He finds 0.011% in his fresh Ca Cl₂ and 0.04% in his carbon. He thinks, however, his porcelain crucible chiefly to blame. He observed

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that tho he had great difficulty with his strontium, he could electrolyse it in an iron crucible with a fresh anode; also that the addition of silica caused the appearance of the effect.

The facts in the present case seem to point to Borchers' theory - that it is a function of the anode current density, - rather than Willner's silica theory. The calcium chloride used showed no silica; a 6 gram sample was used, and 0.002% could have been detected. Samples of the poorest electrolyte showed only 0.10%. This electrolyte had been used for the Goodwin furnace, poured out and used in the Borchers' furnace; was dug out of this with a chisel, swept up and used a second time, and a second time chiselled out and put in the Goodwin furnace. It would seem that this electrolyte ought to have picked up considerable silica, and shown the anode effect, but no anode effects were noticed with it, because it was too viscous to allow a skin of gas to form, and also the current was too high. This last statement requires some ex-

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planation. The anode effect was only noticed with the smaller currents, for the amount of current used in a normal electrolysis was not enough to keep the whole crucible open, perhaps three-fourths of the anode surface being covered with a layer of solid Ca Cl_2 . On increasing the current, since the heat is proportional to the square of the current, the temperature, - and consequently the anode area exposed - increased faster than the current, so that when the entire area of the anode was in contact with fused electrolyte, the current density was much less than before. And not enough current was available to reach the critical current density with the whole of the anode surface open.

The explanation which seems to come from these experiments is substantially the one quoted from Borchers above. Thompson⁽¹⁾ has also given a similar explanation for the anode effect in alumina melts. It may be stated in detail thus:-

(1) Thompson, Electrochem. Metall. Ind., 7, 19, (1909).

19.

Under any particular set of circumstances, for any given electrolyte, there is a critical current density, above which the bubbles of gas will be evolved fast enough to cause them to coalesce into a sheet of gas, thru which the current must arc. This of course cuts down the current density again, but the power is about doubled, and this increased power, together with the fact that the surface of the electrolyte is at the positive (and consequently the hotter) pole of a multitude of arcs, raises the temperature of this skin so far that the conditions are identical with the spheroidal state. At this very high temperature the gas layer may contain volatilized electrolyte.

That the anode effect is a function of the current density is further shown in Fig. 3. If this is so, moving the cathode nearer to a part of the anode should, by increasing the current density at that point, induce the anode effect if other conditions were near the critical point. The effects marked with a cross were ^{so} produced. _A This was not invariably the case, but the great majority

of such attempts were successful. Again, in the run in the Borchers' furnace using a 2" carbon rod as anode, the anode effect was permanent thruout the run. In this connection it might be mentioned that in contradiction to various statements that the evolution of chlorine ceases during the effect, in this run the evolution of chlorine was such as to make existence in the furnace room almost impossible, as the apparatus was too large to arrange any drafts for it. Further, anything which cooled the layer of gas should stop the effect. At the temperature obtained, the graphite disintegrates rapidly where exposed, and on scraping off the loose graphite on the outside of the part of the crucible where the anode effect was taking place, normal conditions were immediately restored. As this layer of loose graphite in a measure protected the crucible against further action, it could not often be attempted, as the crucible would have worn thru. Touching the inside of the crucible with the point of a file was of no effect, perhaps because its heat capacity was too low to produce any great cooling. In confirmation of

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Woehler's statement, pulling out the main switch for an instant destroyed the effect. That the effect does not take place in a new crucible was explained by the difference between the rough surface of a freshly-machined piece compared to the very smooth surface of the crucible after a few runs. The projecting particles pierced the gas layer until they were corroded off by the action of the hot gases - which must combine with the carbon to some extent. That the power is greater during the effect is shown by figures calculated from the data of Fig. 3. During the effect at 4:44, the average power was 3590 watts; during the interval, 1544 watts, during the next effect, 3355 watts, and during the next interval, 1515 watts. That the anode effect was intermittent is explained as follows:- It will be noticed from Fig. 3, that almost all of the effects gradually grow less till they suddenly fall off. This would show that the power is greater, that in consequence of the higher temperature the radiation is faster, and so the crucible slowly cools to the temperature where the skin must break. The decreased power causes still

further cooling and the exposed surface of the anode decreases till the critical current density is reached, when the effect takes place, the increased temperature exposes the anode a little more, and then the cycle is repeated.

By the end of the work on the anode effect the crucible was badly used up and further improvements became necessary. The copper band contact was not very successful, being nearly burned out. The crucible was almost worn thru, due to disintegration from the outside, and also partly from the bottom. To eliminate these two troubles the following crucible was designed, after wasting much time trying to repair the old one.

A 6" length of 5" round graphite was sawn off, a cavity $3\frac{1}{2}$ "X4" turned in one end, and one $4\frac{1}{4}$ "X $1\frac{1}{4}$ " in the other. A hole $1\frac{1}{2}$ "X2" and about $\frac{1}{4}$ " deep was cut in one side near the bottom, and then the lower third was copper plated, inside and out, till a coating heavy enough to solder to was obtained. A lug was made of a short strip of heavy sheet copper bent at right angles, and one-

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half of this was soldered into the hole. The other end thus projected from the crucible and was covered with paraffin. The whole was now placed in the bath, and copper plated till a uniform layer of copper at least $\frac{1}{8}$ " thick was obtained, all the cracks around the lug filled, and any projecting bits of solder covered, so that the lug would be held by the copper even against the twist of the cables if the solder should melt. The paraffin was removed, and all the rest of the copper covered with several coats of asphaltum, each one baked on. A section $3\frac{1}{2}$ " high was cut from a tin can, $6\frac{1}{2}$ " diam. A hole was cut in the bottom and the crucible put thru this, giving an annular space, $\frac{3}{4}$ " wide, around the top of the crucible. A mixture of about four parts carborundum fire sand, two parts fire clay, and one part Ba So₄ was wet up with water glass and rammed in this space, and the whole baked. This crucible has been used in only two runs, but has been satisfactory in every respect and can be recommended for any electrolysis of fused salts.

CASTING METALLIC CALCIUM.

Calcium is a very difficult metal to handle. Though fairly stable at ordinary temperatures, when hot, and especially when melted, it combines with N, O, H, CO₂; alloys with all metals; attacks carbon, silica and silicates. An attempt was made to cast it in fused (chloride). One of the old crucibles was put in a resistance furnace, Ca Cl₂, melted down in it, and then lumps of metal added. It melted and remained floating, covered and protected by a film of chloride. As the melt cooled, however, the surface suddenly cleared off, catching fire in spots, the metal burning very slowly, and the oxide piling up in flower-like masses; then solidifying to a spongy mass of non-coherent crystals. Much of the metal formed carbide at the points where it touched the crucible. This gave no coherent lumps of metal, neither did it allow casting the metal in any form.

A small round graphite crucible was prepared, having a cavity perhaps 2" diam. and 3" deep. Magnesia was

sintered in a resistance furnace, ground up, mixed with Mg Cl₂ solution, and stamped into this around a core, leaving a hole about $\frac{1}{4}$ " in diameter. This was placed in a resistance furnace and heated barely to redness. Ca Cl₂ was dropped in, and rapidly soaked up by the magnesia. After a time small pieces of the metal were added, covered with more chloride, and melted very slowly. Attempts to cast the calcium were entire failures for several reasons. The crucible was too small to give any considerable body of metal. The magnesia was not thoroughly sintered, and the crude method of making the crucible did not give a coherent lining, for the metal was absorbed almost as readily as the chloride. And in attempting to keep the temperature as low as possible, it was kept so low that the melting took so long that the metal had ample time to combine with both the oxygen and nitrogen of the air, and on attempting to use a higher temperature the metal caught fire. Such small portions of the pasty metal as were scraped out were very yellow (the color of the

nitride) - and on dissolving in acid gave a very strong test for ammonia. Tho no success was obtained, it seems that a properly made crucible of lime or magnesia should be the solution of the problem.

S T R O N T I U M .

Only two runs were made with strontium chloride as electrolyte. In the first, the temperature sufficient to melt the chloride was so high that the metal burned almost as fast as formed, and what few shots of metal did separate were molten, so that instead of adhering to the cathode they floated in the solution and were carried to the anode to recombine with the chlorine. The resulting oxide fouled up the bath so that it became relatively infusible. Contrary to Willner's experience, that the anode effect was far more troublesome than in the case of calcium, it was not encountered here at all. This may have been due either to the fact that the whole anode surface was in contact with the liquid, or that it was the first run in a new crucible. After the electrolysis one

small shot of metal about 4 mm. diam. was found.

A second run, in the new crucible, just described above, was more encouraging. At a current of 75 amperes, the flames of burning strontium appeared, while at 45 amperes, the next step on the rheostat, the bath froze up. By alternating between the two, tho mainly at 45 amperes, electrolysis was continued for about an hour. The cathode was raised about 2" in the course of the run, a stick of metal being apparently formed. On removal it was found to consist mainly of carbide and chloride. The carbide was accounted for by the fact that the charge was first melted by passing alternating current thru a small graphite rod, which disintegrated rapidly, filling the bath with finely divided graphite. That the stick conducted the current is perhaps due to the fact that it contained a sponge of metal, for on breaking while fresh and hot, a fine network of yellow lines were seen, which quickly vanished. On standing a day in a dessicator they no longer appeared. On treating a lump of about 5 grams with water, some 225 c.c. of gas were evolved. This was

a mixture of hydrogen and acetylene, but thru some error in the analysis the exact figures obtained are worthless. Further work on this metal is in progress.

It is rather difficult to make a concise summary of this thesis, the work being largely a matter of detail. Some 500 grams of metal were prepared, analysis of which gave the following: Free carbon, 0.17%, Si, None, Fe., 0.01%, Al, 0.03%, Mg, None. This was made on a 1.5 gram sample, so that the results are quite accurate. In general, however, it may be said

I. The published descriptions of apparatus for the preparation of metallic calcium have been elaborated and improved upon, especially the crucible.

II. Some figures for efficiency under adverse conditions are given, and the fact shown that the electrolyte must be pure and the temperature as low as possible.

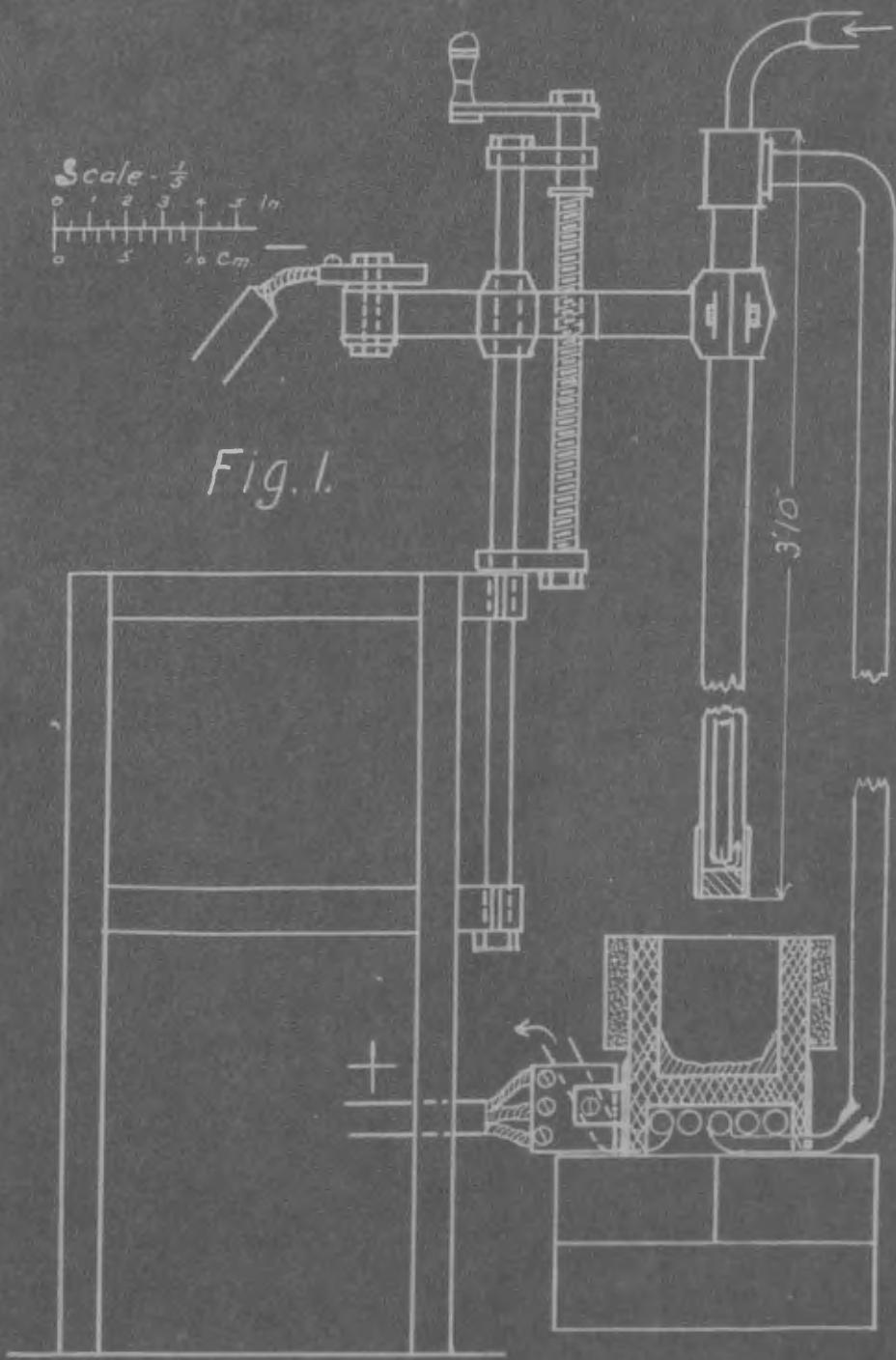
III. The anode effect has been studied in great detail, no other investigator having published complete data of any run; and an explanation given.

IV. Various negative results obtained which may be
of assistance to others in working along the same lines.

This work was undertaken at the suggestion of Mr.
Francis C. Frary, and done under his supervision. I wish
to express my thanks, not only for his many suggestions,
but also for his assistance in a great deal of ^{the} _A actual
work, which was at many times very laborious.

Scale - $\frac{1}{3}$
0 1 2 3 4 5 cm

Fig. I.



Scale - $\frac{1}{2}$
0 1 2 3 4 5 6
C.m.

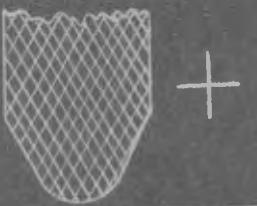


Fig. 2.

