

THE CASTNER SODIUM PROCESS

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CASTNER applied for his patent for manufacturing sodium by the electrolysis of fused caustic soda in 1890, and in 1893 production at Oldbury was at the rate of about 2 tons a week. The plant at Billingham shut down in 1952 and had a capacity of 105 tons a week. The amount of sodium made by the Castner process during the last thirty years of its life in this country amounts to roughly 140,000 tons, and for those who like this kind of thing Dr. Hardie has calculated that this is equal to a block of sodium as big as Cunard Building. The process was worked in many other countries and was, for thirty years of its life, the only way of making sodium commercially. It seemed fitting that the end of a process which had been worked successfully for over fifty years should be marked in some way or other, and the object of this paper is to do so by giving a somewhat more detailed account of the process than can be found in the ordinary text book.

The title of the patent is "Improvements in the Manufacture of Sodium and Potassium." This conventional expression is a modest way of describing a tremendous advance. Castner had previously made sodium by heating caustic soda and his so-called iron carbide to a sufficiently high temperature to distil off the sodium, i.e. above 800°C. This would be an unattractive process today with all our resources of chemical plant and materials of construction, but in the period 1880-90 it must have been a very nasty business indeed. To describe the change from this clumsy, difficult process to the elegant process described in the patent as an improvement, was stating things very mildly. Castner could not, of course, patent the electrolysis of fused caustic soda. Davy had electrolyzed fused caustic soda years before, and the reaction was common knowledge among chemists. Castner's essential claim was that the temperature of the bath should be kept as close as possible to the melting point, and, in any case, must not exceed it by more than 20°C. The following extracts from the patent make it clear what was claimed:

"... I declare that what I claim is:

1. The hereinbefore-described process of manufacturing the alkaline metals which consists in treating the caustic alkali while constantly maintained at a temperature of not more than 20°C. above its melting point to the action of the electric current, substantially as described.

2. The hereinbefore-described process of manufacturing the alkaline metals which consists in submitting the caustic alkali to the action of the electric current, said alkali being kept at such a low temperature that the metal may be separated but not distilled, substantially as described.

3. In apparatus for carrying out the process described in the foregoing claims, the combination with the two electrodes of an interposed screen or gauze and a vessel adapted to receive the reduced metal, the surface area of the electrodes and their distance apart being proportioned to the quantity of current employed so that the bath may be kept at a constant temperature."

If the criterion of a good patent is that it acquires protection for the process without divulging how to make the process work, then Castner's patent must be ranked among the very good ones of this world. The unfortunate person who had to

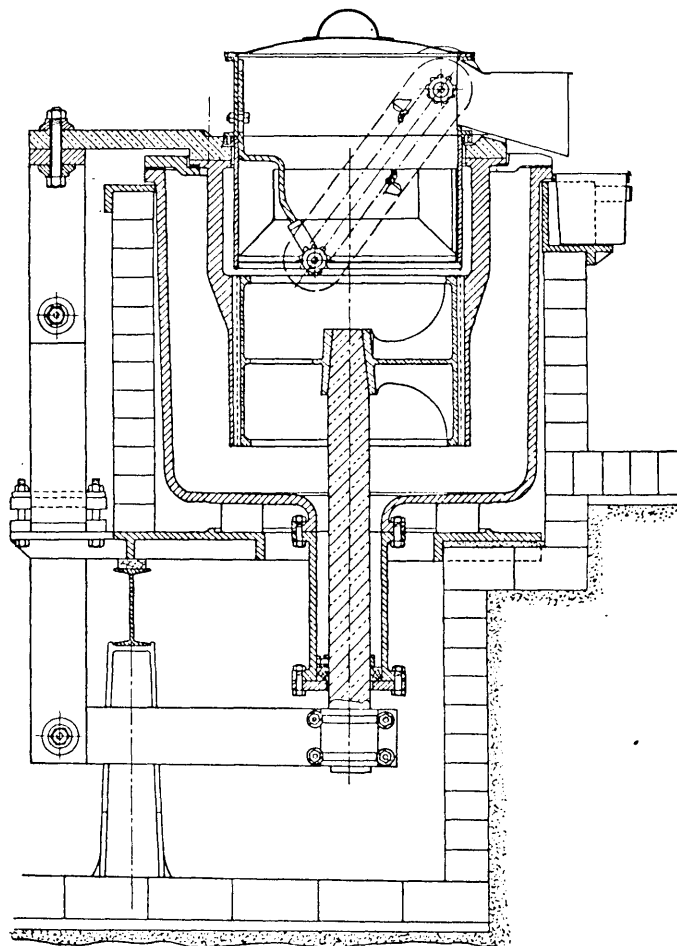


FIG. 1.—Cross-section of pot

run the process with only the text books and the patent specification to guide him was in for a very difficult time.

The apparatus described in the patent has not changed in principle since the beginning of the process. It has increased in size and various bits have been added to it. Improved methods have been adopted for making the electrodes, but a cross-section of the present pot is just like a cross-section of the first one Castner installed. It consists of a cast-iron outer pot which contains the bath and the electrodes. The cathode is of copper and the anode of nickel. In choosing materials of construction regard had to be paid not only to the resistance to chemical attack from fused caustic soda, but also to attack from strong boiling caustic soda solution. When the pot reached the end of its useful life it was taken out of circuit and immersed in boiling water to dissolve the caustic soda remaining in it and so allow the various parts to be taken out. Aluminium makes a very good cathode and is not appreciably attacked by molten caustic, but, of course, it could not be used because it would not resist the boiling-out process. Incidentally, aluminium was of no use as an anode. The current passes momentarily and

Chem. and Ind. (1953) 876-82

then falls to zero—presumably owing to the formation of a film of oxide on the metal.

Both the electrodes were cast of pure metals, and years ago this called for very highly skilled work on the part of the founders. The anodes of pure nickel were cast in a shed in the backyard of a house in Birmingham, and the castings made there in the most primitive conditions were superior to any made by the large firms to whom one had to go when the size of anode required became too big for the small man in Birmingham.

In the last twenty years anodes and cathodes were made from fabricated plate welded into the proper shape. This was only possible with the development of technique for welding pure nickel and pure copper. It was easier and cheaper to get suitable electrodes this way than by casting them.

Once in an experimental pot a cathode of nickel was tried but it never worked satisfactorily and the reason was never discovered. The stem of the cathode went down the leg of the pot and a flange on the stem rested on a wooden ring, which in turn rested on the flange of the pot leg. The cathode was centred by a gauge and was then sealed in position by filling the leg of the pot with molten caustic soda which, after it had set, fixed the cathode for good.

The anode sat on a cast-iron ring, which in turn sat on the rim of the pot. The various parts were insulated from each other by sitting them on pieces of asbestos board. The anode was positioned relative to the cathode by a gauge. Once in position it was fixed by driving wooden wedges between the top ring and the specially arranged rim of the outer pot.

The electrodes were 1 in. apart and midway between them was an iron gauze which allowed free circulation of the bath but kept the molten sodium from straying across to the anode. The gauze was carried by a steel cylinder called "the inner pot" which rested on a recess in the top ring of the anode. It was insulated from the anode by pieces of asbestos which also served to wedge it in position. The inner pot extended practically to the top of the cathode, and there the gauze portion began and extended the full length of the cathode head. The inner pot had a steel cover which fitted sufficiently closely to allow hydrogen to escape and prevent air getting in. This, incidentally, ensured that there was always an atmosphere of hydrogen in the pot, which prevented the metal burning.

The pots were connected in series by copper leads of suitable cross-section, and special leads were employed for bridging over a pot—or "cutting it out" to use the common phrase.

Each pot sat on a cast-iron plate which formed the base of a brick chamber and the top was closed with another cast-iron plate. These plates were obviously enough called "the top and bottom plates" and the pot was insulated from the bottom plate by sitting on insulating bricks and from the top plate by wedges of asbestos. The space between the plates was filled with brickwork so that in effect the pot sat in a brick chamber.

Sixty pots were connected in series and supplied with power at 250 volts. At this voltage no particular precautions had to be taken by the men, as everything was very dry.

In the early days of the process each pot was heated by gas to keep the contents molten. It was quickly found that it was simpler, and in the end no more costly, to rely on the passage of the electric current to keep the bath fluid. This had the added advantage that as the heat was generated in the centre, conditions could be so arranged that there was a skin of solid electrolyte on the walls of the outer pot which served to protect it, to insulate it and to provide a check on the temperature of the bath. When the process began the pots were very small. The cathode was 4 in. wide and the whole apparatus was about the size of a waste-paper basket. As time went on the size increased, and finally the outer pot weighed 1600 lb., had an internal diameter of 39 in. and was 54 in. from the top to

the bottom of the leg. The electrodes were of corresponding size and the pot held about one ton of caustic soda.

In addition to the pots themselves there had to be melting boilers for the fused caustic soda and all the ancillary apparatus, balers to get the metal from the pot, ladles for carrying soda to it, moulds for casting the metal, etc. These will be dealt with in the section describing the operation of the process.

The bath

The process consists in electrolyzing fused caustic soda, and the only additional information provided by the patent is that the temperature of the caustic should not be more than 20° above the melting point. It would seem, therefore, that all that was needed was to fill the pot with molten caustic soda, put the switch in and start collecting the sodium. Castner quickly found that with the caustic soda available to him the pots would not work, and that before his process could be successful he had to find some purer caustic soda. He made this by the well-known mercury-cell process. The electrolysis of fused caustic soda, like other electrolytic reactions, is remarkably sensitive to traces of impurity. The common impurities in caustic soda are carbonate, chloride, sulphate and silicate. Mercury-cell caustic usually contains about 0.5% of carbonate, 0.2% of chloride, 0.02/0.03% of sulphate and about 0.01% of silica. There are also traces of metallic impurities.

Carbonate and chloride are actually beneficial, as will be indicated later. After a period of fifty years it is still uncertain how much sulphate can be tolerated. Pots have worked excellently with 0.4% of sulphate in the bath. About silica there is no doubt. It was found early that silica is deadly, and as this was a prominent impurity in the pre-electrolytic caustic soda it is not to be wondered at that the pots gave a tremendous amount of trouble when the process began.

As the electrolysis proceeds the silicon is deposited on the cathode and interferes with the electrolysis. The amount in electrolytic caustic soda is not sufficient to cause trouble, but the silica along with other impurities accumulates in the bath as the pot grows older and is one of the factors determining its life, i.e. the time from starting up to when it has to be taken out of circuit.

There are traces of many metals even in the pure white finished soda. They are there in parts per million, but only calcium interferes seriously. Metals such as iron, nickel and copper are obviously not harmful, otherwise it would not be possible to use them in the construction of the pot. In any case, metallic sodium precipitates these metals from fused caustic just as sulphur does. In fact, in preparing fused caustic for the sodium process, it was customary to finish it with sodium instead of sulphur in order to keep the sulphate content to a minimum. It was not certain how sulphate affected things, but the safe line was to have as little as possible present. Any of these metals which were present in the electrolyte were thrown out of solution by the sodium which was being made.

Calcium was not thrown out in this way. There is not much known about how much calcium is required to upset the pot, but it is not much, as may be gathered from the following bit of history. About forty years ago the caustic soda used at Wallsend, where the sodium process was located, was made at Castner-Kellner Works, Runcorn. Without warning, the pots at Wallsend started to give trouble. The bath became thick, there were all the ordinary symptoms of flashing in the outer pot, and the yield of sodium fell catastrophically. The whole factory had to be shut down, all the pots washed out and re-set and a new start made. No explanation of this misbehaviour was found at Wallsend. It was found, however, that the people at Runcorn making the caustic had been putting 10 lb. of lime per 10 tons of caustic soda into the liquor, with a view to reducing the corrosion of the caustic finishing pots. It was probable

out not determined, that most of the added lime would eventually appear in the bottoms in the finishing pots, and not in the finished caustic soda. It is certain, however, that the collapse of the sodium process followed the addition of the lime, and when the plant was re-started on soda which had not been treated with lime it worked normally.

Some fifteen or so years later experiments were carried out on single pots, and the rather extraordinary result was obtained that while substantial amounts of calcium carbonate could be added to a pot without upsetting it (the pot worked quite well with 0.046% of CaO in the bath) the addition of calcium chloride rapidly reduced the yield. The matter was never followed up, mainly because there were other more important things to do. Very great care was taken to keep clear of calcium salts. For instance, the risk was never taken of using caustic soda made by causticizing soda ash with lime.

Mercury-cell caustic, therefore, has the necessary freedom from impurities and yet it is unsatisfactory as an electrolyte. If a pot is filled with pure caustic soda it behaves badly. It makes sodium, but in reduced yield, and to the accompaniment of flashing and cracking in the anode part of the pot. It also has a characteristic appearance in the inner pot that can be best described, as the workmen used to describe it, as "having no body in it." It looked thin with the molten sodium spread tightly over the surface which was violently disturbed. In a normal pot there was a uniform froth on the surface and the metal was relatively quiescent.

It was quickly found that the addition of sodium carbonate and chloride to the bath made the pot work a lot better. The amounts varied. At one time the bath started life with 5% of carbonate and 2% of salt. Later it was found that a bath containing 10% of salt and 5—10% of carbonate allowed a higher current to be put through the pot without ill effect. That was the mixture in use when the process was wound up.

It is not known why carbonate and chloride were beneficial. If they reduced the solubility of sodium in the bath they would be advantageous indeed, but there are no data on the solubility of sodium in fused caustic of varying composition. It is known that carbonate lowers the melting point—the lowest point being 285° c. when the carbonate content is about 20%. It is also known that the electrical resistance and the viscosity of fused caustic soda increase with increasing carbonate content. The effect of sodium chloride is not so marked. The melting point rises slowly but the effect of adding 10% is small. Two practical effects of working with 10% of salt were that higher current could be used and the solid soda around the mouth of the pot became very much harder.

Pure caustic soda is a softish solid but soda containing 10% of salt is glassy hard. This is quite an important point, as will be seen later.

As the soda fed to the plant contained carbonate, chloride sulphate and silica, the composition of the bath changed steadily. The life of a pot depended on many things, and a troublesome pot might have to be taken out quite early. Generally speaking, however, a life of seventy to eighty days was expected, and by that time the bath contained round about 20% of salt, 15—20% of carbonate, 0.3% of silica, and 0.2—0.3% of sulphate. It was very discoloured and had a large quantity of black material in suspension. This was mostly oxides of iron, copper and nickel precipitated from the caustic soda by the sodium. At any one time, therefore, the bath in the pots of a set of sixty would range in composition between the starting and finishing limits above described. The knowledge of the best mixture for the process is almost purely empirical, having been established by trial and error. There was no theoretical information to work from, and it was quicker and easier to proceed empirically than to examine the whys and wherefores of the business.

The electrolysis

The theoretical amount of sodium that can be obtained by electrolysis is 0.86 gram per ampere-hour. The defect of the Castner process, and the defect which had probably more to do with its demise than anything else, is that the maximum possible is 0.43 g./amp.-hr. What happens in effect is that half of the current is used in making hydrogen which cannot be collected and is, therefore, wasted.

When the current is passed sodium is liberated at the cathode and hydroxyl ions at the anode. These hydroxyl ions combine to form water and oxygen. Most of the oxygen comes off through the feed hole of the pot but some stays in solution. Oxygen is quite appreciably soluble in fused caustic soda and it can be shown that this has much to do with the action of fused soda on metals. The moisture stays in the fused soda and is carried round into the cathode section where it reacts with the sodium, giving caustic soda and hydrogen. There may be more elaborate and subtle explanations of what goes on, but for running the process this one served for its lifetime. In the early days Dr. Ewan tried to prevent the water getting back into the cathode compartment by coating the gauze between the electrodes with a paste of alumina and sodium aluminate. This diaphragm allowed ions to pass through, carrying the current, but prevented wet soda getting back. Until the diaphragm collapsed it worked, and current efficiencies considerably higher than 0.43 were obtained. This was at least supporting evidence for the idea that the physical passage of water from one part of the pot to another was what was happening. Practically the idea was useless. The voltage between the electrodes was increased so much that in spite of the improved current efficiency the power efficiency, which is what mattered, was lower than with the ordinary pot. Furthermore, the diaphragms were relatively costly and did not last very long. The experiment did, however, give some clue as to what went on.

In practice a pot was working well if it gave an efficiency 0.4 g./amp.-hr. and a power yield of 90 g./amp.-hr. The current used depended obviously on the size of the electrodes, and a current of 8500—9500 amperes was used at Billingham. The cathode current density was approximately 7 amp./sq. in. If a higher current was used the pots began to work "hot". This was a good enough description. Although the temperature went up only a few degrees the solid soda on the sides began to melt, sodium started to dissolve in the bath and there was trouble generally.

There was always difficulty in running a process consisting of a large number of small units all differing somewhat from each other. The composition of the bath varied from pot to pot and the current had perforce to be the same for them all. The process makes sodium, hydrogen and oxygen. As already mentioned, the hydrogen cannot be collected but by the exercise of considerable ingenuity some success was achieved years ago in collecting the oxygen, only to find that oxygen at atmospheric pressure was not worth very much, and certainly not worth what it cost to collect it.

Operation of the process

The following is a brief description of how the process was worked. This will fall into two parts. From 1892 to 1920 the main operations were carried out by hand and the layout of the plant was governed by that fact. From 1920 to 1930 many of the hand operations were eliminated or minimized so that when the process was transferred from Wallsend to Billingham in 1930/31 the new Castner sodium plant, consisting of the large pots already referred to, could be laid out entirely differently from its predecessors.

In what may be called "the first era" the layout was determined by the fact that the metal was baled out of the pot by

and carried in a steel container to a casting table; the soda replenishing the bath was carried in bowls from a melting pot to the sodium pot, and when a set of pots had to be set up all the soda had to be carried to them by hand. It was obvious that to meet these conditions distances had to be as short as was practicable.

Sixty pots, therefore, were arranged in four rows of fifteen each with the melting boilers for caustic soda a short distance from one end and the casting tables for the metal some distance from the other. Space had to be left for moving pots in and out and getting drums of caustic to the melting boilers.

Another consideration was air space. The electrolyte was at a temperature of 300/310° C. and the working conditions in the shed were warm. For this reason alone it was necessary to leave some space between the pots and the boilers holding the stock of molten caustic soda—another source of heat.

The sixty pots were set up and connected together. It was not possible to fill more than fifteen at one time because by the time the fifteenth was filled some two hours had passed and the first one was so nearly solid that any further delay would have meant that the current would not pass when the switch was put in. The fifteen pots were connected to a motor generator and started up. Fifteen more were filled and connected in series with the others, and so on until the whole set was on load. The molten soda doctored with carbonate and salt was carried to the pots by a string of a dozen or so process men, each of whom carried a steel bowl with a long handle holding 14 lb. of soda. This was very arduous work and by the time fifteen were filled the men had had enough. The starting up process, therefore, usually took the better part of 24 hours.

The process men had to be specially clad for working on this process on account of the risk of burns from fused caustic soda and molten sodium.

When the current was first switched on the pots crackled and sounded like machine gun fire, and it was some hours before they settled down to working quietly. Once all the lids were on and the pots were quiet the men could settle down to their normal duties. In this pre-1930 period two men looked after

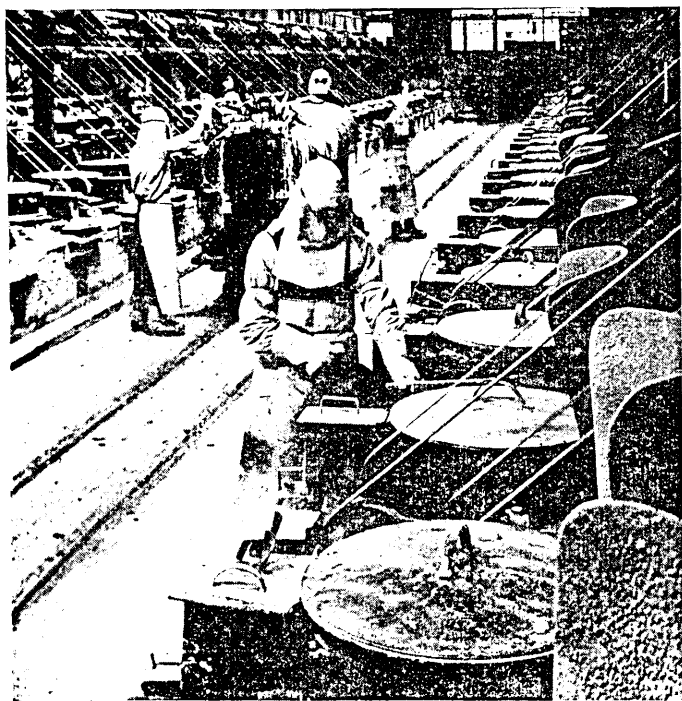


FIG. 2.—General view of process building and plant



FIG. 3.—Baling sodium from a pot

fifteen pots and were occupied roughly 50% of their time. Their main duties were to bale out the sodium every half hour, to feed the pot with molten soda every hour, to clear solid soda away from the mouth of the pot every hour, to clean the inner pot every shift, to keep the bench clean and tidy, and to give extra attention to pots that needed it.

Getting the sodium by baling it out with a perforated ladle which had holes of such a size that the sodium was retained while the molten caustic soda ran through was one of the ingenious dodges for which Castner was famous among the people who worked with him. The problem of getting the sodium from the pot in a decent state of purity was a difficult one, and it had to be solved if the process was to be really successful. Castner applied himself to the problem and solved it in his characteristic way—simply and effectively. The men were issued with oval ladles which were poked but not pierced. The men punched the holes themselves and knew just how big to make them. With these balers sodium was quickly removed from the pot practically free from caustic soda. It was poured into a two-handled iron vessel which when full was carried to the casting table at the end of the bench. There the metal was poured from the carrying vessel into a vertical rectangular mould where it was allowed to solidify. Any caustic soda which had got in with the metal solidified long before the sodium, and being much denser settled to the bottom of the molten metal. As a final safeguard the end quarter of an inch of each stick was cut off and re-melted. The rest of the stick of sodium was then free from caustic soda.

In all this handling of sodium there was danger of dampness owing to the deliquescent nature of the materials. Sodium, oxide and caustic soda are all hygroscopic. The results of ladling molten sodium into a damp mould could be, and occasionally were, very serious. The panacea was oil—quantities of it. Tanks of a light gas oil were at each casting table, and any vessel, mould or drum which had to receive sodium, molten or solid, was rinsed thoroughly with oil immediately before using. Another trouble was fire. Molten sodium takes fire fairly easily and once burning is exceedingly difficult to put out. The standard

method when the surface of some molten sodium started to burn was to pour liberal amounts of oil on to it. The oil flared up and the metal beneath the burning oil was vigorously stirred so that the burning metal was covered with the other metal, and the oil burning blanketed the surface. This was a little spectacular but was quite effective. For some purposes sodium was wanted free from oil and in such cases moulds etc. had to be laboriously dried by heating, and if the sodium did start to burn vigorous stirring was all that could be done. If in desperation oil had to be used, then that sodium was discarded for that particular use.

The other duties were straightforward enough. The clearing of the mouth of the pot—"cutting down" was the term used by the men—was a very variable duty. If the pots were working slightly warm there would be no solid soda to chisel away, whereas if they were cold the solid soda at the mouth would be plentiful and, owing to the salt in it, very hard indeed. In such circumstances "cutting down" was a very strenuous occupation.

The attention given by the men to their duties affected the working of the plant. It was essential that the pot should be cleared of metal every half hour. If the baling was done carelessly and metal left in the pot, then it began to dissolve and before long there was trouble. If, in the extreme case, metal was not taken from the pot a stage was reached where so much

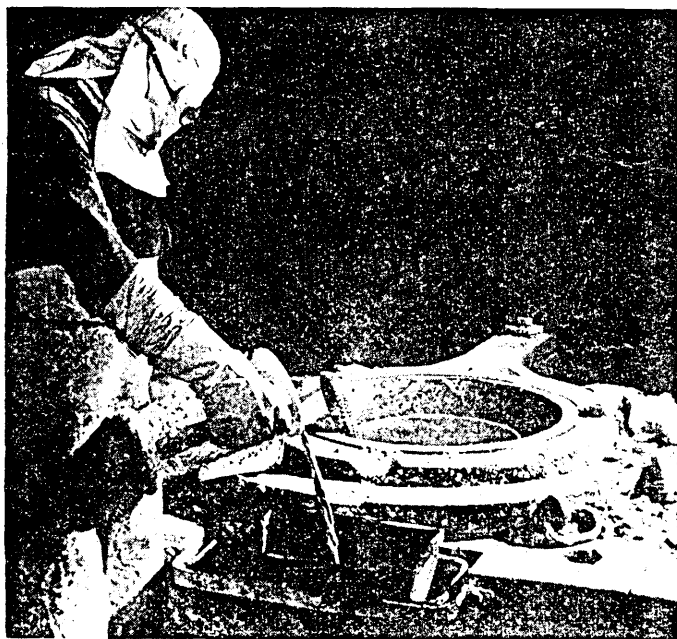


FIG. 4.—Pouring molten sodium into a mould

sodium was dissolved in the bath that the current was carried without any electrolysis at all. To use the very expressive description of the men, the pot was "dead" and no word could describe its appearance more accurately.

This solution of sodium in fused caustic soda is most highly corrosive, and it attacks steel very vigorously. A pot has been seen in which the soda in the inner pot was as black as ink and completely still with 4000 amp. going through it. The soda contained 1.5% of iron in solution—an unheard of amount in ordinary caustic soda. Such a thing was most exceptional, but careless baling did certainly affect performance very seriously. If feeding were neglected and the level of the electrolyte was allowed to drop, a point could be reached where the gauze would be exposed, resulting in hydrogen and sodium burning in the pot.

Another effective way of upsetting a pot completely was to clear the inner pot carelessly. The spray on the walls above the electrolyte was scraped off into a ladle and taken away. If the walls were scraped back into the pot the pot started to crackle and flash in the outer pot. Analysis of the spray gave no clue to its behaviour. As might have been expected, the composition did not differ very much from that of the electrolyte, and probably the workmen's theory was as good as any. They maintained that the pot was clearing itself of undesirable muck by throwing it out as spray, and if the spray was put back the pot was upset. The pots in their behaviour displayed so much individuality that it was not to be wondered at that the workmen took a somewhat anthropomorphic view of them.

In 1917 women workers were successfully employed on the potting process. Instead of two men there was one man and two women. The man did the heavier work of cutting down, feeding and inner-pot cleaning. The women did the baling and casting of the metal. The only trouble, apart from the eternal trouble connected with running mixed factories, was to get them to be sufficiently careful over the protective clothing. Some of them thought nothing of doing the last bale at the end of the shift in high-heeled shoes and bare necks.

A special section of men was employed to assemble the pots—"set them," to use the men's term for it. They were responsible for taking them out of circuit and moving them with a crane to a part of the shed where the molten contents could be poured out into iron receptacles. The pot was then put in a wash tank containing weak caustic soda liquor heated with live steam. The solid soda dissolved out and finally the electrolyte could be taken out. The soda from the pots was dissolved in water and from the liquor, in a suitable recovery plant, solid soda was obtained, testing 70% of Na_2O was recovered for sale. The theoretical caustic soda usage is 1.74 lb. of soda per 1 lb. of metal. In practice the usage of high-grade soda was 2 lb. per 1 lb. and the nett usage after allowing for recovered caustic soda was 1.8—1.9 lb.

This process of cutting pots out, emptying, washing up, dismantling and reassembling could all be done in two days—if wanted, a pot could be out one day and in the next. If the electrolyte in the pot were allowed to go solid, it could then take a week or more. The greatest catastrophe in any plant using fused electrolyte is, for one reason or another—usually by failure of the current—for the pots or cells to solidify. It was generally reckoned that it took three months to get a set back on line again, using every available resource. Two to three hours without current was as much as dared be risked. After that the chances of getting enough current through to heat up the battery were very slender. On one occasion at Wallsend owing to a power failure there was only power for one set out of twelve. This was the position for some eighteen hours, and the sets were kept alive by running them alternately for an hour at a time. They were not making much sodium after eighteen hours of this treatment, but when power was available for both it was possible to bring them back into tolerable condition. The alternation would have been to lose a set for at least three months.

These remarks about the operation of the process applied to the process as worked up to 1920. Between the years 1920 and 1930, Dr. Fleck made two very important changes. The first of these was to demonstrate, for the first time in this country, at any rate, that fused caustic soda could be pumped like any other liquid. This made it possible to alter the arrangements for filling up a set of new pots and for feeding the pots once they were working. There was no need, in laying out the plant, to have regard to the distance the process men had to carry ladles of molten caustic soda.

When a row of pots had to be filled a three-inch steel pipeline was run along the top of the pots and from there to the submerged

ump in the caustic soda melting boiler, wherever that happened to be. There were tees in the pipe over every inner pot, through which soda could pour into the pot. There was a flange on the delivery part of the tee to which was attached a steel plate with a handle. When the pot was full enough the flow was stopped by sliding the plate over the opening of the tee and bolting it tightly to the flange. This crude device was effective provided the job was tackled resolutely and an occasional splash of molten caustic did not matter. The first time the system was tried out the mistake was made of starting with the furthest-away pot, the idea being to open the tee outlets as the work progressed down the bench. Opening them to allow a flow of soda seemed more attractive than closing them to stop a flow of caustic. Unfortunately, the effect of expansion was overlooked. So just as the soda began to flow into the pot the pipe reared itself off the bench, took on a substantial bend and fell over on to the floor, spewing caustic soda all over the place. The next time a start was made with the nearest pot first, which meant warming the pipe up gradually. There was no trouble apart from joints leaking here and there, and this system of filling up a set of new pots was established.

When the plant at Billingham, which was shut down last year, was laid out there were two long benches of thirty pots instead of four of fifteen. This saved floor space and copper leads and was advantageous in many ways. As in the case of all other improvements, there was a price to pay. The system necessitated filling all of the sixty pots at one session, and that meant the job had to be done in under three hours—otherwise the first pots would be too solid to start. This had all been worked out, but it depended, of course, on the pump behaving itself. If the pump seized, as it did at times, another one had to be got in pretty quickly. Fortunately, these hazards were successfully avoided.

Being able to pump caustic allowed better arrangements to be made for feeding. Soda was pumped from a boiler into a lagged tank which was carried on an electric truck and fitted with a special discharging valve. This truck delivered caustic soda to the men attending the pots, much as milk is delivered. The men had a light steel jug and they drew the soda they wanted as the truck stopped opposite the pot. All carrying of soda was thus done away with except for the two steps from the truck to the feed point. This was essential, of course, to the adoption of thirty-pot benches.

The second improvement made by Dr. Fleck was the design of an apparatus to be fitted on top of the pot for removing the sodium mechanically. It was called "The Dredger" and that, in fact, was what it was. Without going into detail, it was a little bucket elevator with gauze buckets which lifted sodium and caustic, allowed the caustic to drain back, and at the turn of its travel at the top threw the sodium into a little receiving compartment from where it ran into a mould. This eliminated hand-baling and carrying vessels of molten metal to the casting table. Both were unpleasant jobs, and carrying the metal was dangerous. Two fatal accidents occurred through men spilling sodium over themselves. The moulds stayed until they were full and were then lifted on to a flat-topped truck which travelled round the set collecting moulds of metal to take to the casting tables.

This improvement again greatly improved the labour usage—and again, like other improvements, a certain price had to be paid. The presence of the dredger made the important job of cleaning the inner pots much more difficult. In fact, it became impossible to do it properly, and part of the price of the improvement was in shorter working lives for the pots.

This was the point the process had reached when it was shut down last year. The improvements mentioned, larger

pots, pumping molten soda and baling mechanically, reduced labour from 90 man-hours per ton to 30 man-hours per ton.

Recovery of waste sodium and caustic soda

There was a constant production of what were known as "skimmings"—a mixture of metallic sodium, sodium oxide, caustic soda and oil. This stuff contained enough sodium to make it worth working up. It was a special job by itself where a solitary man melted the material up in an iron pot. Liberal quantities of oil were used to stop the metal burning, and the whole operation was conducted in an atmosphere of flames and smoke. In this job there was ample opportunity for the sodium to dissolve in the caustic soda, and here it could be seen how corrosive is this solution. The pot was of cast iron, 3 in. thick, and lasted three months. The steel bowl used to work the material and draw out the molten sodium lasted three days. This barbarous business was abandoned when the Billingham plant was put up. An incidental benefit of mechanical baling and delivering directly to the mould was to reduce the amount of "skimmings" to a negligible quantity.

The recovery of caustic soda has already been referred to.

Troubles

The following are some of the troubles met with and the methods employed in dealing with them. Major troubles such as the emergency created by a power failure and the effect of a harmful impurity in the caustic soda have been referred to. These were troubles which affected the working of the factory as a whole, and they were rare. The daily troubles were those arising from the misbehaviour of individual pots, and it was remarkable what a variation in behaviour could occur among a number of pots all, so far as one could arrange it, working under the same conditions. The symptoms were nearly always the same. For convenience in referring to them use will be made of the term "inner pot" for the cathode compartment where the sodium normally accumulated, and the term "outer pot" for the anode compartment where the oxygen was evolved and into which the make-up caustic soda was fed. The symptoms of trouble were: flashing and crackling in the outer pot, with occasional blobs of molten sodium floating about; and melting away of the solid caustic which normally was found under the top ring and around the sides of the pot. This behaviour was described by the men as "working hot," and once again their description could not be bettered although such measurements of temperature as could be made between a hot pot and a cold pot showed at most a few degrees difference.

For all that, pots generally tended to work "hot" in the summer and "cold" in the winter. When pots working hot became out of hand they could reach the condition already referred to as "dead." The standard method of bringing them to life was to pour water into the outer pot. This process was accompanied by much spluttering, and if there were any blobs of molten sodium about there could be an alarming firework display.

The method was very effective. A "dead" pot could be seen to liven up as the water reacted with the sodium dissolved in the caustic soda. The soda in the inner pot, from being perfectly still, would rush round, gas would start to come off, the pot would crackle, sodium would appear in the inner pot and for a while all would be well. This process of destroying the symptoms did not, however, always remove the cause of the trouble, and such pots were liable to relapse unless the real cause was found and put right.

Another method of cooling off a hot pot was to short-circuit it with a $\frac{3}{4}$ -in. iron rod which shunted part of the current and

gave the pot a chance to cool down and accumulate its lining of solid caustic. A more drastic method was to cut the pot out of circuit for an hour or so to let it cool down properly.

Occasionally a pot became so hot that the solid soda cementing the cathode leg into the leg of the outer pot would melt and the whole contents would run out. This was not infrequent, and in most cases the pot emptied itself quietly and broke the circuit. It had to be short-circuited before the current could be put on the set again.

On two occasions it was not so quiet. Once a pot ran out and a blob of sodium must have started an arc between the electrodes, because in this case the set continued to work with the empty pot roaring and flaring like a furnace. The current was shut off at the sub-station and the electrodes in the pot were found in a partly fused condition. A current of 4000 amp. had been passing and this made quite a fat arc flame. On another occasion a pot partly short-circuited by a $\frac{3}{4}$ -in. iron rod ran out, and for a brief span the whole 4000 amp. passed through the rod. It was all very quiet. The rod quickly turned white hot and quietly disappeared. Occurrences like these were rare, but they lent an interest to life.

A source of frequent trouble was the distortion of the gauze or movement of the inner pot to which the gauze was fastened. In either case the result was the same, the gauze touched the cathode on one side and on occasions the anode on the other. It acted partly as a short-circuiting conductor and partly as an intermediate electrode. Everything went wrong under these circumstances, with things being made in the wrong places. Experienced men developed remarkable gifts for feeling for tight places with a flat rod which they put down the inner pot between the gauze and the cathode. The space between the anode and the gauze was inaccessible. By feeling with this rod tight places could be found and corrected by moving the inner pot slightly. It was quite striking at times to hear a noisy pot suddenly become quiet when the inner pot was moved slightly. In extreme cases an inner pot and gauze would be replaced while the pot was working, and when everything failed there was nothing for it but to take the pot out and replace it with another.

When the weather was cold, and occasionally for no apparent reason, pots worked cold. In this case an excessive amount of solid caustic formed on the walls, and sometimes there was enough on the bottom to seal the bottom of the electrodes and the gauze. This completely upset the normal circulation of soda from one electrode compartment to the other. The worst effect was that it became difficult to get make-up soda into the pot. Whatever was put in frothed out again with the result that the level in the pot fell until the danger point was reached where the gauze was exposed. This condition was difficult to deal with for an occasional pot. A general condition could be corrected by increasing the current, but it was impossible to raise the current on a single pot. This trouble, however, was much less frequent and less troublesome than the opposite one of the pots becoming hot.

The main secret of dealing with troubles such as have been described was attention by the men. Additional baling could work wonders with a pot working hot. Frequent small feeds could help in the case of a pot working cold. The difficulty was always that, having set the current to suit the majority of the pots, it was not possible to alter it to suit a few bad ones.

An endeavour has been made to give a picture of the working of the process. It was, perhaps, a strenuous process for modern industry but it worked well for half a century, which is no small tribute to the man who invented it.

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SULPHURIC ACID INDUSTRY

THE following information is contained in a statistical summary of matters concerned with the sulphuric acid industry issued quarterly by the National Sulphuric Acid Association, Ltd., to its members:

Summary of monthly returns, United Kingdom, April 1 to June 30, 1953

(a) Sulphuric acid and oleum—tons of 100% H_2SO_4

	Chamber only	Contact only	Chamber and contact
Stock, April 1, 1953	26,417	32,603	59,020
Production	161,120	298,739	459,859
Receipts	31,992	22,642	54,634
Oleum feed	—	1212	1212
Adjustments	-116	-119	-235
Use	99,843	115,799	215,642
Despatches	89,195	206,577	295,772
Stock, June 30, 1953	30,375	32,701	63,076
Total capacity represented	200,080	365,400	565,480
Percentage production	80.5%	81.8%	81.3%

(b) Raw materials—tons

	Pyrites	Spent oxide	Sulphur and H_2S	Zinc concentrates	Anhydrite
Stock, April 1, 1953	130,762	214,597	51,327	86,246	550
Receipts	94,102	66,408	57,334	37,504	45,965
Adjustments	-1072	612	1,223	-37	—
Use	95,922	68,712	61,845	39,998	45,635
Despatches*	309	17,379	105	—	—
Stock, June 30, 1953	127,561	195,526	47,934	83,715	880

* Including uses for purposes other than sulphuric acid manufacture.

Consumption of sulphuric acid and oleum in the United Kingdom, April 1 to June 30, 1953

Trade uses	Tons 100% H_2SO_4
Accumulators	2347
Agricultural purposes	450
Bichromate and chromic acid	3052
Bromine	4120
Clays (fuller's earth, etc.)	2226
Copper pickling	911
Dealers	2755
Drugs and fine chemicals	3234
Dyestuffs and intermediates	15,752
Explosives	7761
Export	542
Glue, gelatine and size	184
Hydrochloric acid	13,085
Hydrofluoric acid	2708
Iron pickling (including tin plate)	22,818
Leather	882
Lithopone	3068
Metal extraction	996
Oil refining and petroleum products	16,054
Oils (vegetable)	2538
Paper, etc.	1403
Phosphates (industrial)	399
Plastics, not otherwise classified	5336
Rayon and transparent paper	55,332
Sewage	2766
Soap and glycerine	7088
Sugar refining	171
Sulphate of ammonia	70,617
Sulphates of copper, nickel, etc.	5985
Sulphate of magnesium	1344
Superphosphates	119,740
Tar and benzole	4705
Textile uses	5540
Titanium oxide	40,994
Unclassified	34,532
Total	461,295