ANALYSES REQUIRED FOR AN ELECTROLYTIC ALKALI WORKS.

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WHILE in the main the analytical methods for an electrolytic alkali works are the same as used in the old processes of caustic and bleach manufacture, we have found in practice that the modifications given below facilitate the operations required. Some of the analytical methods necessarily have to be varied from those of the old processes because of the inherent difference in the electrolytic method of manufacture.

The analyses given below, which are used for a plant working a mercury cathode process, may be discussed under the following heads: (1) Raw Materials; (2) Factory Control; (3) Finished Products.

RAW MATERIALS.

Limestone.

Determinations: Silica, ferric oxide and alumina, calcium carbonate, magnesium carbonate. These determinations are carried out in the usual way. A limestone as high as possible in calcium carbonate is required.

Slaked Lime.

Determinations: Water and carbon dioxide.

Water.—The workmen in the lime house become so expert in the slaking that they can generally tell by the physical characteristics when just enough water has been added, hence a water determination is not often required. When a sample comes to the laboratory it is quartered down quickly to about one ounce, and one gram heated for one hour over a blast-lamp. The loss in weight is reported as total water.

Carbon Dioxide.—This is rarely determined and usually amounts only to one- or two-tenths of a per cent. The determination is made in the usual manner with a Schroetter or other apparatus used in the analysis of carbonates.

Salt.

Determinations: Insoluble in water, calcium sulphate ($CaSO_4$, $2H_2O$), calcium chloride ($CaCl_2,6H_2O$), magnesium sulphate ($MgSO_4$), magnesium chloride ($MgCl_2,6H_2O$), sodium sulphate (Na_2SO_4), ferric oxide and alumina, and sodium chloride.

We make the analysis on the sample which has been dried over night in the steam oven at 100° to 105° C., and calculate the above salts according to the laws for the distribution of acids and bases, the determinations being ferric oxide and alumina, lime, magnesia, sulphur trioxide, and chlorine. Since the ferric oxide and alumina are usually very small in amount, they are not regarded in the distribution of acids and bases, but reported as weighed.

A salt low in sulphates and lime salts is required, as these accumulate and foul the electrolyte.

Water.

Determinations: Total solids and complete analyses of inorganic constituents. These determinations are made in the usual manner. A water low in sulphates and lime salts is required for the same reason as above.

FACTORY CONTROL.

Caustic Liquor.

Determinations: Sodium hydroxide and sodium chloride. Five cc. of the liquor as it comes from the cell is taken, the alkalinity determined by normal sulphuric acid with phenolphthaleïn as indicator, then a few drops of neutral potassium chromate solution are added and the sodium chloride determined by decinormal silver nitrate.

In this way, individual cells tests are made once each day and a test on the average liquor from each unit of forty cells is made every two hours throughout the twenty-four.

Spent Brine.

Determinations: Specific gravity at 60° F., free chlorine, sodium hypochlorite, sodium chlorate, sodium chloride, sulphur trioxide, iron and aluminum oxides, lime, magnesia and mercury. About one liter of the brine is required for the tests. The reresults are reported in grams per liter.

Specific Gravity.—The specific gravity is best determined by cooling a portion of the brine to 60° F., and taking the reading with a Westphal or Mohr balance.

Free Chlorine.—Pipette out two portions of brine of 50 cc. each into 8-oz. Erlenmeyer flasks, add 10 cc. of a saturated solution of potassium iodide, shake well, stand five minutes, titrate the liberated iodine with decinormal hyposulphite, using starch solution as indicator. Multiplying the number of cubic centimeters "hypo" solution required by 0.00355 × 20 gives the number of grams of free chlorine per liter.

Sodium Hypochlorite.—Two portions of brine of 50 cc. each are pipetted into 200 cc. beakers and the free chlorine + sodium hypochlorite determined with decinormal arsenious acid (Penot's method), using drops of starch solution and potassium iodide on a spotting plate as indicator. Deduct from this the number of cubic centimeters of "hypo" required for the free chlorine, and multiply the remainder by 0.003724 × 20, which gives the number of grams of sodium hypochlorite per liter.

Sodium Chlorate.--For this determination we prefer the following modification of the method given in Sutton's "Volumetric Analysis."

Take either the solutions from the sodium hypochlorite titration or pipette out two portions of 50 cc. each into 8-oz. Erlenmeyer flasks, and run in the number of cubic centimeters decinormal arsenious acid solution as determined above. Weigh out a quantity of C. P. ammonium ferrous sulphate in excess of the chlorate (unless it is known about how the brine is running in chlorate, several trials may be required to find this weight). Add the ferrous salt to the solution in the Erlenmeyer flask, close the mouth of the flask with a small funnel and place on a hot plate or sand-bath. Add 15 cc. concentrated sulphuric acid through the funnel (about 1 cc. at a time) slowly, allow to come to a gentle boil and remain so for three or four minutes. Then cool the solution and titrate the excess of ferrous salt with potassium bichromate. Multiply the amount of ferrous iron present by 7 to obtain the weight of ammonium ferrous sulphate in excess. Deducting this from the amount weighed out gives the ferrous salt oxidized by the chlorate decomposition, and this multiplied by 25.51 × 0.001775 × 20 = number of grams of sodium chlorate per liter, or the same result is obtained by multiplying the weight of iron oxidized by 0.3169 × 20.

Sodium Chloride.—Instead of making the titration for sodium chloride in the same solution in which the chlorates were determined, as recommended by Sutton, we find it quite as accurate and more rapid to proceed as follows: Take 50 cc. of the cooled solution just after reading the specific gravity, and dilute to 1 liter with distilled water. Pipette out portions of 10 cc. each and titrate with decinormal silver nitrate, using about 8 drops of a 10 per cent. solution of neutral potassium chromate as indicator. Multiply the reading in cubic centimeters by 100, deduct from this the number of cubic centimeters of arsenious acid solution required in the free chlorine + sodium hypochlorite titration, which is a sufficiently accurate correction for the free chlorine and sodium hypochlorite present; the remainder multiplied by 0.00585 × 20 gives the number of grams of sodium chloride per liter.

Sulphur Trioxide.—Pipette out 2 portions of 50 cc. each, add to each 50 cc. water with 3 cc. concentrated hydrochloric acid, and boil violently to completely decompose all hypochlorites and chlorates. When the smell of chlorine has disappeared, add slowly to the boiling solution 10 cc. of saturated barium chloride solution which have been diluted to 50 cc. and heated to boiling. Allow to stand until the precipitate settles, filter, wash with hot water to free precipitate from chlorides, dry, ignite, and weigh barium ulphate, and from this, calculate the sulphur trioxide.

Ferric Oxide and Alumina, Lime, and Magnesia.—Two portions of 100 cc. each are pipetted out, 50 cc. water with 3 cc. concentrated hydrochloric acid added to each, and the solutions then boiled violently until the smell of chlorine has disappeared. The precipitation and weighing of ferric oxide and alumina, the determination of the lime, and the precipitation and weighing of the magnesia are conducted the same as in an ordinary limestone analysis.

Mercury.—Two portions of 50 cc. each are pipetted out, 50 cc. of water with 3 cc. concentrated hydrochloric acid added to each, and the solutions boiled violently for several minutes. When the smell of chlorine has disappeared, pass hydrogen sulphide through the hot solution until the mercury is all precipitated. Filter on a Gooch filter that has been previously dried at 100° C. for one hour and weighed. Wash the precipitated mercuric sulphide with hydrogen sulphide water until all the sodium chloride is removed, then with alcohol, next with ether, then with carbon bisulphide until all the free sulphur is removed. Finally wash out the carbon bisulphide with ether, then follow with alcohol, dry at 100° C. for one hour and weigh as mercuric sulphide. Calculate to mercury and report as such.

A complete analysis of the spent brine as above is made each week on a sample which represents an average of all the cells. Individual cell tests on the brine for sodium chloride alone are made once per day. A complete brine analysis with the exception of the magnesia can be made by one chemist in about four hours. The magnesia, precipitated as ammonium magnesium phosphate, is allowed to stand over night and finished the next morning.

Chlorine Gas.

Determinations: Chlorine and hydrogen.

These tests are made with an ordinary Orsat-Muencke gas analysis apparatus, having two pipettes filled with a solution of potassium iodide and caustic potash which serve for the chlorine absorption (the small amount of carbon dioxide gas present is negligible), while a palladium tube is attached for absorbing the hydrogen.

These tests are made on the gas once each day.

FINISHED PRODUCTS.

Caustic Soda.

Determinations: Sodium hydroxide + sodium carbonate, and sodium chloride (other determinations to make a complete analysis are rarely asked for).

The sample, which usually comes to the laboratory still hot, should be taken from the bottle, piece by piece, and broken quickly in a mortar to pieces no larger than a pea, bottling again as quickly as possible. When all is broken, mix sample thoroughly by turning the bottle over and over. The bottle should not be more than two-thirds full to insure a thorough mixing. Take a weighing bottle, which has been previously dried and weighed, and fill it with caustic from the mixing-bottle, close bottle, and reweigh. Empty the caustic from the weighing-bottle into a beaker, dissolve and pour caustic solutions and rinsings into a liter flask. Dilute nearly to the mark, cool under the tap to a temperature approximately that of the room, dilute to the mark, mix thoroughly by turning the stoppered flask end over end.

Sodium Hydroxide + Sodium Carbonate (Total Na_2O).—Pipette out 50 cc. of the caustic solution into a beaker, add 4 or 5 drops of methyl orange indicator and titrate with normal sulphuric acid.

Repeat the titration on 50 cc. portions until a constant reading is obtained. Multiply the number of cubic centimeters used by 0.031 × 20 and divide by the weight of caustic taken; this gives the per cent. of total Na_2O in the sample, *i. e.*, the Na_2O existing as carbonate and hydroxide, the small amount existing as sulphide and sulphite, etc., being disregarded.

Sodium Chloride.—Pipette out two cc. portions of the caustic solutions into beakers of 250 cc. capacity, carefully neutralize with nitric acid, and titrate the sodium chloride with decinormal silver nitrate as usual.

The caustic soda analysis is usually limited to a determination of the total Na_2O, which is made on a sample from each pot as it is finished.

Bleaching-Powder.

Determinations: Available chlorine, water, carbon dioxide, total chlorine.

Available Chlorine.—This test is best made by the old arsenious acid titration (Penot's method).

Water.—We have been unable to find a perfectly satisfactory method for this determination, but have used the following:

One gram of the bleaching-powder is quickly mixed with about 5 grams of dry copper oxide and placed in a porcelain boat near the back part of a 12-inch combustion tube. Beyond the boat the tube is filled with scrap sheet silver mixed with cement silver which should be in a spongy condition. A weighed Geissler bulb containing sulphuric acid is attached for absorption of the water. Two similar bulbs are attached at the other end for drying the air which enters the tube. The tube is heated gently at first, dry air being aspirated slowly through the apparatus, finally the heat is raised immediately under the boat as high as the tube will stand and kept so for an hour and a half. The sulphuric acid bulb is detached and weighed in the usual manner.

This method of retaining the chlorine is based on the following reaction:[1]

$$Ca(OCl)_2 + 4CuO = CaCl_2 + 2O_2 + 2Cu_2O.$$

The silver serves to retain any chlorine that may escape from the boat.

Carbon Dioxide.—For this determination a train was arranged

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[1] Richter's "Inorganic Chemistry," p. 370.

as follows: First, two potash bulbs for removing the carbon dioxide from the air entering the apparatus; second, a flask of about 100 cc. capacity fitted with a stop-cock funnel for introducing the acid for decomposition; third, three Geissler bulbs filled with a nearly saturated potassium iodide solution for absorption of the evolved chlorine; fourth, a U-tube containing fused calcium chloride lumps free from caustic for absorption of water from the gas before it enters the potash bulb; fifth, a weighed potash bulb for the absorption of the carbon dioxide.

One gram of the bleaching-powder is placed into the decomposition flask and about 15 cc. of dilute hydrochloric acid (1 : 4) dropped in from the stop-cock funnel, a current of air being slowly aspirated through the apparatus. The chlorine is all absorbed in the first and second potassium iodide bulbs, the third remaining colorless. To remove the carbon dioxide that is absorbed by the potassium iodide solution, the aspiration of the air is continued for two hours after the bleaching-powder is decomposed. While there is a possibility of iodine vapor being carried over into the potash bulb, we have had no such trouble as the third potassium iodide bulb, remains colorless throughout the operation. The potash bulb is detached and weighed in the usual manner.

Total Chlorine.—One-half gram of the bleaching-powder is reduced with arsenious acid solution as in the available chlorine test, then neutralized with nitric acid and the chlorine determined in an aliquot part with decinormal silver nitrate solution; this gives the chlorine existing as hypochlorite and chloride. A determination of the chlorates present by the method under spent brine analysis, is made on one-half gram of the sample. It is better, however, to use hydrochloric acid for the chlorate decomposition here. For these results the total chlorine is calculated.

Of the above determinations, the available chlorine is the only one made in daily practice. This analysis is made on the chamber that is "up to strength" just before the charge is withdrawn for packing.

Nearly all the above analyses are made at this laboratory for Mr. B. E. F. Rhodin, managing director of the Canadian Electro-Chemical Co., to whom we are indebted for many suggestions and courtesies.

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