Other salts of soda which are of importance on account of their acid constituents—nitrate, silicate, phosphate— are dealt with under Nitrogen, Silica, Phosphorus.

The estimation and analysis of alkalis are sufficiently dealt with at the close of the article Potassium.

*Soda Manufacture.*

The ancients probably did not know soda in other than its native forms, and till about the end of the 18th century potash was, of the two alkalis, the more abundant and generally used substance. In­deed it was not till well into that century that the chemical dis­tinctions of the alkalis were established ; they were previously spoken of indifferently as nitrum, natron, kali, alkali, and soda, names simply meaning a fixed alkali. Soda has properly a separate history only from 1736, when Duhamel established the fact that common salt and mineral alkali have the same base,—a body different from the salt of tartar or vegetable alkali. Yet soda, from both mineral and vegetable sources, had long previously been used in Europe, the Arabs having probably brought into Spain a knowledge of the alkali and its sources. Apart from the trona and soda lakes, &c., already alluded to, the only source till the close of the 18th century was the ashes of certain plants which grow on the sea-coast and in salt-impregnated soils. These plants, principally species of *Salsola* and a few other genera of the natural order *Atripliceæ,* on incineration yield an ash containing in some cases about 50 per cent. of carbonate of soda. The ash of these plants, fluxed by red heat into a pasty mass and broken into con­venient lumps, forms the barilla of commerce, which in former times was a product of the first importance on the shores of Spain, Sicily, Sardinia, and other coasts of the Mediterranean. In 1834 as much as 12,000 tons of barilla were introduced into England from Spain alone, and, in spite of the cheapness of artificial soda, the manu­facture of barilla is still—or at least was till recently—carried on at various localities on the Mediterranean. On the west coasts of Scotland and Ireland large amounts of impure soda carbonate were obtained from the kelp burned from certain sea-weeds ; but the introduction of artificial soda early extinguished that industry, although in connexion with the production of iodine and other products a small quantity of sea-weed soda continues to be made in Scotland till the present day.

The increasing price of potash salts and the discovery of Duhamel led to strenuous attempts to produce the carbonate from common salt. In 1775 the French Academy of Sciences offered a prize of 2400 livres for a practical method of converting salt into soda. But it was never awarded, although the problem was soon triumphantly solved. Indeed in that same year Scheele succeeded in making soda from common salt by means of litharge. Several claims were made for the prize, the first being based on a process invented by a Benedictine monk, Malherbe, in 1778, which was worked with some success for several years. Some time about or before 1787 De la Métherie proposed a plan for calcining with charcoal the sulphate prepared from chloride,—an impracticable proposal, because nearly all the resulting product is sulphide.@@1 But this proposal has historical importance, because from the pub­lished account of it Le Blanc received in 1787, according to his own statement, the first suggestion of his process,—probably the most valuable and fertile chemical discovery of all times. Nicolas Le Blanc, born at Issoudun (Indre) in 1753, was private surgeon to the duke of Orleans. He was a chemist as well as a surgeon, and the prospect of the Academy prize attracted his attention to the soda problem. He added to the sulphate and charcoal mixture proposed by De la Methérie a certain proportion of chalk, and by fluxing the mixture in crucibles succeeded in effecting the desired transformation. The chemist D’Arcet and his assistant Dizé, having recognized the soundness of the process, the duke of Orleans, early in 1790, agreed to provide a capital of 200,000 francs for working the process. In September 1791 the National Assembly granted Le Blanc a patent for fifteen years, and under the superintendence of Le Blanc himself, with Dizé and Henri Shée, the steward of the duke of Orleans, a work was established at Saint Denis. But on the fall and execution of his patron Le Blanc, and all others owning and working soda processes, were ordered to resign them to the state for the public benefit, he receiving the miserable compensation of 4000 francs. In 1800 his works were reconveyed to him, but in 1806, broken in hope, health, spirit, and resource, he perished by his own hand in a workhouse.

Le Blanc’s process continued to hold the field against all compet­ing schemes till within the last few years, and that essentially in

@@@1 It is well established, however, that carbonate of soda can be pro­duced in this manner. It was Liebig, we believe, who showed that the first step in the Le Blanc process is approximately thus — 2Na2SO4 + 6C = Na2S2 + Na2CO3 + 5CO, only the disulphide and the carbonate on continued heating act on each other and on the carbon to form Na2S.—Na2S2 + Na2CO3 + 2C = 2Na2S + 3CO.

its original form. Owing to the raw materials employed in it and the products evolved, it became the basis of a series of import­ant industries, and many interesting collateral processes have been grafted on the manufacture. Its origin was contemporaneous with the introduction of bleaching-powder (see Chlorine, vol. v. p. 678), and the hydrochloric, acid given off in the conversion of chloride into sulphate of soda became the raw material of that industry, the two processes being worked in conjunction. Since the days of Le Blanc many other methods for more directly manu­facturing artificial soda have been proposed ; but only one—the so- called “ ammonia process ”—has seriously threatened to supplant it.

*Le Blanc's Process.—*This consists of two stages. In the first stage common salt is converted into sulphate of soda by the action of sulphuric acid. At first acid sulphate of soda is produced thus— 2NaCl + H2SO4 = HCl + NaHSO4 + NaCl ; but subsequently at a sufficient temperature the acid sulphate decomposes the remainder of the salt thus—NaHSO4 + NaCl = Na2SO4 + HCl, so that all the chlorine is expelled as hydrochloric acid with formation of normal sulphate of soda. In the second stage the sulphate mixed with limestone and coal (charcoal in Le Blanc’s original proposal) is calcined in a reducing flame, whereby a mixture of sulphide of calcium (CaS) and carbonate of soda is formed, oxygen being gen­erally supposed to pass off as carbonic oxide, CO. According to Lunge, however, the gas produced consists chiefly of carbonic acid, so that the reaction should correspond essentially to the equation Na2SO4 + 2C + CaCO3=Na2CO3 + CaS + 2CO2. The sulphide of calcium being practically insoluble in water and only very slowly acted on by a solution of carbonate of soda at temperatures under 45° C., the carbonate is extracted by systematic lixiviation with water at a temperature under that limit and is recovered from the solution by evaporation. If an excess of lime is used, more or less of the soda assumes the caustic form (NaHO). All crude soda-ash lyes contain some caustic alkali besides the following impurities :— chloride of sodium, sulphate of soda, sulphide of sodium combined with sulphide of iron into a soluble green compound which occa­sions much trouble to the manufacturer. This solution contains also occasionally cyanide or ferrocyanide of sodium, produced by the action of cyanide on the soluble form of sulphide of iron.

*Salt Cake Making.—*The conversion of the salt into sulphate, called “ salt cake,” is effected by means of sulphuric acid of about 60 per cent. (chamber acid), and may be, and still very commonly is, carried out in reverberatory furnaces having flat soles of cast iron, attached to one end of which is a pan of the same material. The waste heat from the reverberatory furnace is utilized to heat the charge placed in the pan, where the first part of the change is effected, the reaction beginning briskly with evolution of copious fumes of hydrochloric acid immediately the acid and salt are mixed. Before the Alkali Act of 1863 hydrochloric acid was freely allowed to escape through the stalk with the smoke and fire gases, carrying destruction to the vegetation of vast tracts around the works ; but now all the acid is everywhere carefully collected, both because it is a source of profit and from sanitary considerations. Hence in modern “open roasters,” as these reverberatory furnaces are called, the pan and the calcining sole are separated, so that the comparatively pure and undiluted fumes from the pan can be led away and collected by themselves, leaving the mixed air, fire gases, and acid fumes from the furnace hearth to be separately dealt with. In another class of furnace, called a “blind roaster,” the calcination of the half- finished sulphate is carried out in a muffle, so that none of the hydrochloric acid is mixed with air and fire gases. Certain ad­vantages attend each class of furnace. In working these hand- furnaces there is much unpleasant manual labour, to avoid which mechanical furnaces have been devised, in which the stirring of the charge, &c., is accomplished by machinery. The first mechanical roaster actually used was patented by Jones & Walsh in 1875. In it the whole operation from beginning to end is carried out on the sole of a large cast-iron pan heated from above. Through the roof of the chamber enclosing the pan passes a vertical shaft geared to rotate, to which are attached four horizontal arms, and to these slanting rods are fixed which terminate in scrapers. These scrapers are fixed at different lengths from the shaft centre, so that when the shaft is in motion they pass through and turn over the whole of the charge strewn over the sole of the pan. The acid is passed into the pan by a pipe from a tank situated above the roaster. The hot mixture of fire gases and acid fumes is led through a long pipe to cool down before reaching the condensers.

*Hargreaves's Process* for making sulphate without the direct use of sulphuric acid is based on the employment of sulphurous acid obtained by the ignition of pyrites aided by air and steam. In this way Mr Hargreaves may be said to get his sulphuric acid *ex tempore.* The process has only been elaborated as the result of a most extensive series of investigations and experiments carried out in conjunction with Mr Robinson, their first patent having been obtained in January 1870. The reaction on which the process de­pends may be thus formulated—2NaCl + SO2 + H2O + O = Na2SO4 + 2HC1. The salt used is rendered porous by first moistening it with water and then redrying it by passing it through a hot-air channel