chloride (Ag2S + 2NaCl + 4O from the air = 2AgCl + Na2SO4). The mass, along with certain proportions of water, scrap-iron, and mercury, is placed in barrels, which are then made to rotate about their axes so that the several ingredients are forced into con­stantly varying contact with one another. The salt solution takes up a small proportion of chloride, which in this (dissolved) form is quickly reduced by the iron to the metallic state (2AgCl + Fe = FeCl2 + 2Ag), so that there is, so to say, room made in the brine for another instalment of chloride of silver, which is reduced in its turn, and so on to the end,—the metal formed uniting with the mercury into a semi-fluid amalgam. Of this the bulk at least readily unites into larger continuous masses, which, on account of their high specific gravity, are easily separated from the dross mechanically. The amalgam is pressed in linen bags to eliminate a quantity of relatively silver-free liquid mercury (this of course is utilized as such in subsequent operations), and the remaining solid amalgam is subjected to distillation from iron re­torts, whereby its mercury is recovered as a distillate while a more or less impure silver remains in the retort. This process, after having been long wrought in Freiberg with great success, is now super­seded there by the Augustin method (see below), but it survives in some other places, as, for example, the Washoe or Comstock district in the Sierra Nevada (United States). It is not used in Chili, Peru, and Mexico because of the scarcity of fuel.

The *Mexican process,* though far less perfect than that of Freiberg, evades this difficulty. It was tried for the first time, if not actually invented, by Bartolomeo de Medina in 1557. It was adopted in Mexico in 1566 and in Peru in 1574, and is in use in both countries and in Chili to this day. The stamped ore is ground into a fine paste with water ; this paste, after having been allowed to dry up a little in air, is placed on a stone floor along with a quantity of salt, and the two are trodden together by mules. On the following day there are added certain proportions of “magistral” (a kind of crude sulphate of copper made by roasting copper pyrites) and of mercury, and the mules are kept going until the silver is as far as possible converted into amalgam, which takes from fifteen to forty-five days. The rationale of the process is not quite understood. According to Boussingault, the cupric chloride (formed by the salt from the sulphate) chlorinates part of the sulphide of silver, thus—

2CuCl2 + Ag2S=2 AgCl + S + Cu2Cl2, and the cuprous chloride formed acts upon another portion of sulphide of silver, thus—

Cu2Cl2 + Ag2S = 2 AgCl + Cu2S,

and in this way all the sulphide of silver is gradually converted into chloride. The chloride is reduced to the metallic state by the mercury (AgCl + Hg=HgCl +Ag) with formation of calomel, the metallic silver uniting with the surplus mercury into amalgam. The calomel is allowed to go to waste.

The *Augustin process* of silver extraction is only a peculiar mode of metallifying and collecting the silver of an ore after it has been by some preliminary operation converted into chloride or sulphate. Either salt is brought into solution—the chloride by means of hot brine, the sulphate by means of hot water, acidified with oil of vitriol ; the solution is separated from the insolubles, and made to filter through a bed of precipitated copper. The copper reduces the silver to metal, which remains on the bed as a spongy mass, while an equivalent quantity of copper chloride (or sulphate) passes through as a solution. The silver sponge is col­lected, freed from adhering copper by muriatic acid in contact with air, and then sent to the furnace. From the copper liquor that metal is precipitated in its original form by means of iron.

The silver furnished by any of these methods is never pure, even in the commercial sense. A general method for its purification is to fuse it up with lead and subject the alloy to cupellation (see Lead, vol. xiv. p. 376). Cupel-silver is apt to contain small quantities of lead (chiefly), bismuth, antimony, copper, and more or less of gold, of which metals, however, only the first three are reckoned “contaminations” by the metallurgist. They can be removed by a supplementary cupellation, without added lead, at a high temperature. Addition of lead would remove the copper likewise, but it is usually allowed to remain and the alloy sent out as cupriferous silver, to be alloyed with more copper and thus con­verted into some kind of commercial “ silver ” (see below). If gold is present to the extent of 0∙1 per cent. or more, it is recovered by treatment of the metal with nitric acid or boiling vitriol. The gold in either case remains as such ; the silver becomes nitrate or sulphate, and from the solution of either salt is recovered by precipitation with metallic copper. Although nitric acid is the more expensive of the two parting agents, it is often now preferred because photography has created a large demand for nitrate of silver. Compare Gold, vol. x. p. 749.

For the “ incidental ” extraction of silver from essentially base-metallic ores the method in the case of all lead ores' is simply to proceed as if only lead were present,

and from the argentiferous lead produced to extract the noble metal by one of the processes described under Lead (vol. xiv. p. 376-7), while for the treatment of sulphureous copper ores one method is so to smelt the ore (with, if neces­sary, an addition of galena or some form of oxide of lead) as to produce a regulus of lead and a “mat” of sulphide of copper, (Cu2S), which latter should contain as little lead as possible. The silver follows chiefly the lead, and is extracted from it by cupellation ; but some silver remains in general even with a lead-free mat. Compare account of the Lautenbach process under Lead.

A modern mode of extracting the silver from a copper mat is to roast it at a very low temperature, so as to produce a relatively large proportion of metallic sulphate, and then to destroy the bulk of the sulphate of copper by a judiciously-regulated higher tem­perature. The silver all remains as sulphate, which is extracted by hot dilute sulphuric acid and wrought by the Augustin method.

Very interesting is the process which was patented by Claudet for the remunerative extraction of the few hundredths of a per cent. of silver contained in that kind of cupriferous iron pyrites which is now used, almost exclusively, for the making of vitriol. The “cinders,” as returned by the vitriol maker, are habitually worked up for copper by roasting them with salt and lixiviating the roasted mass with water, when the copper dissolves as chloride, Cu2Cl2 and CuCl2. The silver goes with it, but for its precipita­tion no method was known until Field found that silver dissolved as AgCl in a chloride solution can be precipitated exhaustively by addition of the calculated proportion of a soluble iodide, as AgI. Claudet’s process is only an adaptation of Field’s discovery. After having diluted the copper liquor with a certain proportion of water· he adds the weight of iodine, calculated from the assay, as solution of iodide of zinc, which produces a very impure precipitate of iodide of silver. From it he re-extracts the iodine, by treatment with zinc and dilute sulphuric acid, as iodide of zinc, which is used over again. The “silver precipitate,” which now contains its silver as metal mixed with a large quantity of (chiefly) sulphate of lead, goes to the metal-refiner, who treats it as a lead ore.

*Chemically Pure Silver.—*Even the best “fine” silver of commerce contains a few thousandth-parts of copper or other base metal. To produce perfectly pure metal the most popular method is to first prepare pure chloride (by apply­ing the method given below under “Chloride” to a nitric solution of any kind of ordinary “silver”), and then to reduce the chloride to metal, which can be done in a great variety of ways. One way is to mix the dry chloride intimately with one-fifth of its weight of pure quicklime or one-third of its weight of dry carbonate of soda, and to fuse down the mixture in a fire-clay crucible at a bright red heat. In either case we obtain a regulus of silver lying under a fused slag of chloride—2AgCl + (CaO or Na2CO3) = 2Ag + (CaCl2 + O or 2NaCl + CO2 + O). The fused metal is best granulated by pouring it from a suffi­cient height, and as a thin stream, into a mass of cold water. A convenient wet-way method for small quantities is to boil the recently precipitated chloride (which must have been produced and washed in the *cοld)* with caustic soda-ley and just enough of sugar to take away the. oxygen of the Ag2O transitorily produced. The silver in this case is obtained as a yellowish-grey heavy powder, which is easily washed by decantation ; but it tends to retain unreduced chloride, which can be removed only by fusion with carbonate of soda.

Stas recommends the following process as yielding a metal which comes nearer ideal purity. Slightly cupriferous silver is made into dry nitrate and the latter fused to reduce any platinum nitrate that may be present to metal. The fused mass is taken up in dilute ammonia and diluted to about fifty times the weight of the silver it contains. The filtered (blue) solution is now mixed with an ex­cess of solution of sulphite of ammonia, SO3(NH4)2, and allowed to stand. After twenty-four hours about one-half of the silver has separated out in crystals ; from the mother-liquor the rest comes down promptly on application of a water-bath heat. The rationale of the process is that the sulphite hardly acts upon the dissolved oxide of silver, but it reduces some of the oxide of copper, 2CuO, to Cu2O, with formation of sulphate SO4(NH4)2. This Cu2O deoxi­dizes its equivalent of Ag2O, forming Ag+Cu2O2, which latter is reduced by the stock of sulphite and reconverted into Cu2O which now acts upon a fresh equivalent of Ag2O ; and so on to the end.