THE MacMURTRY-ROGERS PROCESS

Continued from May 15th Issue.

Moreover, it seems probable that the small amount of water present near the zone of combusion aids materially in the desulphurization, acting in some way as a carrier of oxygen from hot material to the cooler material near the hot material; the effect being to slightly increase the quantity of oxygen present and so cause more rapid combustion, with consequent increase of temperature. To take the simplest case first:—

In the desulphurization of regule, if attempting to desulphurize this when dry and in a converter, very little action takes place; if water is added, metallic copper is readily produced. It was proved, in 1904, that this reaction takes place readily at a temperature just below the melting point of copper, as is evident from the porous structure of the product, which cannot have been completely fused.

Gautier* has recently observed this reduction of copper from cuprous sulphide by water vapor, but at a *white* heat; he formulates the reaction as:—

$$Cu_2S + 2\,H_2O = 2\,Cu + SO_2 + 2\,H_2.$$

This may possibly be the only reaction when only water vapour is present. When air is also blown in, sulphate of copper and oxides of copper can be shown to be formed in large quantities; these react with unaltered sulphide in the well-known manner. It seems also possible that some hydrogen peroxide may be formed thus:—

$$Cu_2S + 2O_2 + H_2O = Cu_2O + SO_2 + H_2O_2.$$

This hydrogen peroxide may quickly decompose at a lower temperature and give rise to a rapid evolution of heat at the point where it decomposes; owing first to the increase in the percentage of oxygen in the gas mixture at that point; and second, to the heat given out in the decomposition of the hydrogen peroxide. Any hydrogen formed by Gautier's reaction will burn higher up the charge and so transfer heat from the zone of combustion; some hydrogen appears to burn at the surface of the charge fairly long, and hot flames are seen above the hottest points on the surface.

The above conclusions have not, so far, been definitely proved, but have served very well as a working hypothesis. One can, however, be quite sure, from the nature of the product, that the ordinary reactions between oxides and sulphides and sulphate of copper can be carried out without melting these substances or the copper produced.

If the cuprous sulphide contains nickel sulphide, very little nickel is reduced, although both nickel oxide and sulphate are produced. In the ordinary reverberatory roasting process some nickel is reduced and a smaller amount in the bessemerizing of molten copper matte containing nickel. It seems to follow that the maximum temperature for the reactions—

$$2\,NiO + NiS = 3\,Ni + SO_2 \text{ and}$$
$$Ni\,SO_4 + NiS = 2\,Ni + 2SO_2.$$

is well above the melting point of copper; whereas the equivalent reactions with the copper compounds readily take place at slightly below this temperature. Steinhart has pointed out that it is not possible to reduce molten nickel sulphide by blowing air through it, as nickel silicate is produced.* In this process the nickel oxide and sulphate produced in the blowing operation readily form silicate when the product is melted down on a sand bottom, and give a slag with considerably more nickel in proportion to copper than is the case with the regule under treatment.

When a mixture of sulphides of copper and iron is treated, desulphurization proceeds rapidly if both water and silica are added, but not at all if either of these constituents is absent. Gautier states (*loc. cit.*):—

$$3\,FeS + 4\,H_2O = Fe_3O_4 + 3\,H_2S + H_2.$$

and also that

$$2\,Fe_2O_3 + 7\,H_2S = 4\,FeS + 3SO_2 + 7\,H_2.$$

when air is used in addition it is obvious that this hydrogen will burn, as also will the H_2S. It seems as if Fe_2O_3 is only a product of the reaction where the temperature is low. In a well-burnt charge of matte or ore, in this process. Fe_2O_3 is only seen at the side and top of the cake, that is where it has been cooled by radiation. If Fe_3O_4 is formed, one can understand that it readily parts with 1 atom of O, giving FeO—thus:—

$$Fe_3O_4 = 3\,FeO + O.$$

This atom of oxygen would help in the oxidation of FeS, and

$$FeS + O + O_2 = FeO + SO_2$$

The latter reaction would be very intense and may be a factor in heating up the particles to the point at which FeO and SiO_2 combine. This reaction is very important, and gives rise to a further evolution of heat, and any small portions of ferrous silicate formed will, in consequence, enhance the action in the neighborhood. In practical work, this formation of ferrous silicate and consequent sintering, can be seen extending outwards from the centres where the silicate formation first takes place. In this connection it is quite possible that water also acts as a carrier of oxygen by the alternate formation and decomposition of hydrogen peroxide, thus:—

$$FeS + H_2O + 2O_2 = FeO + SO_2 + H_2O_2$$
$$FeS + H_2O_2 + O_2 = FeO + SO_2 + H_2O.$$

and it seems possible that wherever oxidation takes place at a high temperature in the presence of air *and* water vapor, when the reaction requires an odd number of atoms of oxygen the other atom of oxygen from the molecule or molecules of oxygen will combine with water to form H_2O_2. This view has been brought forward by Armstrong and others in connection with the oxidation of carbon and carbonic oxide.

In the treatment of ore by this process the reactions involved are very similar to those occurring with matte, except that the passage of the zone of combustion upwards is preceded by the distillation of sulphur from pyrite and chalcopyrite. This sulphur must be allowed to escape to some extent, otherwise it interferes with the progress of the reaction by forming a viscous layer of ore and molten sulphur. With both ore and matte charges the time factor is very important.

The reaction must proceed so rapidly that, at the zone of reaction, a sufficiently high temperature is kept up for the formation of ferrous silicate; otherwise ferric oxide is formed and decreases the amount of active oxygen in its neighborhood, when a diminution of temperature takes place, and causes a patch of unsintered material to be formed. If much Fe_2O_3 is formed at any point it does not appear possible to reduce it. The formation of ferrous silicate aids very materially in getting a product low in sulphur, as well as in sintering the material; for it probably acts as a carrier of oxygen to any particles of ferrous sulphide that may be originally included in it.

*Abstracts Jour. Chem. Soc., 1906, p. 548.

*Trans. Vol. XV., p. 233.