XXXIX. Memoir upon the de-sulphuration of metals

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The constituent parts of this water are the following :

		Contents in one Gallon.	In one Pint.
		Grains.	Grains.
Carbonate of lime	-	2.5	0.3125
Muriate of soda	-	9.75	1.21875
Sulphate of magnesia		8.1	0.3875
Sulphate of soda	- -	8	1
Carbonate of iron	-	0.25	0.03125
Sulphate of lime	-	7.75	0.96875
		<hr/> 31.35	<hr/> 3.91875
		Cubic inches.	Cubic inches.
Carbonic acid gas	-	7.25	0.90625
Atmospheric air	- -	5	0.625
		<hr/> 12.25	<hr/> 1.53125

[To be continued.]

XXXIX. *Memoir upon the De-sulphuration of Metals.*

By M. GUENIVEAU, Engineer of Mines.*

AMONG the number of metallic sulphurets which nature presents to us, there are several the decomposition of which is very important in the arts : the sulphurets of iron, copper, lead, mercury, &c., give place to metallurgical processes highly deserving of the attention of chemists.

The nature and properties of these compounds are well known, since chemists have so frequently made them an object of inquiry. The facts, however, collected in laboratories have never been carefully compared with those furnished by the workshops, although it is very well known that the latter description of experiments furnish the most useful results ; and the theory of various operations to which we subject the sulphurets, has not kept pace with the rela-

* From the *Journal des Mines*, vol. xxi. p. 5.—Jan. 1807.

tive progress of science. It is my intention, in this Memoir, to supply what is wanting in this respect : for this purpose, I have made various experiments, and collected several observations long known : to these I have added some reflections peculiar to myself, and have deduced from their examination, consequences which may be productive of some changes in the ideas generally entertained respecting the treatment of the metallic sulphurets.

§ I. *Of the Action of Heat upon the metallic Sulphurets.*

The action of *heat* upon the metallic sulphurets should be first examined, because it is to be met with in all the operations by which we seek to decompose these substances : in order to appreciate it in a precise manner, I have made choice of experiments and observations in which this action is entirely isolated, which is worthy of observation ; for it is because we have not analysed the effects produced by several causes, that we have been led, in metallurgy, to ascribe to *caloric alone* a de-sulphurating power, which it does not seem to possess in any great degree.

The sulphurets of mercury and of arsenic are volatilized in close vessels, when they are exposed to a temperature somewhat raised. The sublimed sulphuret is frequently altered in its colour ; and the experiments of Messrs. Proust and Thenard show that this change is the consequence of a variation in the proportion of the elements of this compound.

The native sulphuret of iron (pyrites of iron) undergoes a partial decomposition only from the caloric : by distilling it in a retort, we cannot extract from it the half of the sulphur which it contains *. In Saxony, the distillation of pyrites upon a large scale never yields more than from 13 to 14 per cent. of sulphur †.

These facts not being sufficient to decide my opinion upon the effects of heat, because all the experiments which have come to my knowledge were made at a tempera-

* Proust, *Journal de Physique*, tome liii.

† Schkutter, tome ii. p. 228, of the French translation.

ture a little raised, I proceeded in the following manner: I put into a crucible, pyrites of iron pulverized; covered it with charcoal in powder, and heated it in the forge for an hour; I found a mass still preserving all the characters of pyrites; it seemed to have been completely melted, and retained two thirds of the sulphur contained in the natural pyrites. This experiment being repeated, left me in no uncertainty upon the effects of heat *by itself* upon sulphuret of iron, and I thought I might conclude, that, whatever be the temperature, these effects produce a partial decomposition.

Sulphuretted copper and pyritous copper, submitted to the action of heat, produce effects analogous to those observed with respect to iron: the distillation of the pyritous copper furnished but very little sulphur: these two kinds of minerals of copper may in short be considered as mixtures of the sulphurets of copper and of iron, and the sulphur which heat separates from it proceeds almost entirely from the sulphuret of iron.

The sulphuret of lead, or galena, is one of those minerals the treatment of which is most various: all chemists agree in regarding it as composed of sulphur and lead only, in the proportion of 15 of the former, and 85 of the latter. I was the more careful in observing the effects of caloric upon the galena, because, by trying to separate the sulphur from it by this agent, I expected to obtain lead in a metallic state, the weight and fusibility of which render the re-union very easy. It was, besides, very easy for me to operate without the contact of atmospheric air.

I put into a retort 30 grammes of galena reduced to powder, which I heated for two hours, but not so strongly as to make it agglutinate: a very little sulphuric acid only was disengaged, produced by the action of the air of the vessels, and I perceived no sulphur sublimed at the neck of the retort. I increased the fire for about two hours more, until both the galena and the vessel which contained it had undergone a kind of fusion. The sulphur volatilized in this second part of the operation was in so small a quantity that it was not possible for me to detach and weigh it: the re-

sidue was of a metallic lustre; it was agglutinated, and did not contain an atom of ductile lead*.

The heat not having been very strong in this experiment, I submitted to the fire of a forge some pulverized galena, placed in a crucible, and covered with charcoal in powder. I found a mass which had been melted, and similar to what is called *matte de plomb* by the French metallurgists; there was no lead free from sulphur, but only some parts of the button were a little ductile. Analysis convinced me that there remained about three fifths of the sulphur contained in the galena. I attributed a part of the loss of 27 per cent., which it had undergone by the action of the fire, to the volatilization of the sulphuret of lead itself; for the loss owing to the separation of the sulphur could not exceed six per cent. at most.

The galena therefore undergoes but a very incomplete decomposition from heat.

I shall not particularize the sulphurets of zinc, antimony, &c., because I do not know a sufficient number of experiments for determining, in a certain manner, the effects which heat produces upon them: analogy, however, inclines me to think that it does not completely decompose them.

All the facts I have presented seem to me to establish, that the action of caloric alone upon the metallic sulphurets, and particularly upon those of iron, copper, and lead, is confined to their taking from them a small portion of the sulphur which they contain, and afterwards in melting and volatilizing them.

§ II. Of the simultaneous Action of Heat, and atmospheric Air, upon the metallic Sulphurets.

The metallurgic operation which has for its object the de-sulphuration of the metals is known by the name of *roasting*. Most of the authors who have spoken of it do not seem to have recognized any other agent in the decomposition except caloric; and even those who since the

* There are few chemists who have not made this experiment with similar results. I may here remark, that if the heat had been long enough continued, and in the open air, the *galena* would have been completely roasted.

new chemical theories have remarked the influence of the atmospheric air, have never regarded it as essential*. The experiments I have detailed having shown how the action of heat alone is insufficient for decomposing a metallic sulphuret, we must necessarily ascribe to the oxygen of the atmosphere the greatest share in the de-sulphuration of the metals by *roasting*. The affinities of sulphur and of metallic substances for this principle render this assertion very probable; it is besides proved by the chemical examination of the produce of all the roasting, as well as by the way in which the operation is conducted. In place of seeing in the roasting of the sulphurets the volatilization of the sulphur, produced *by a well managed heat*, it will be the decomposition of a sulphuret by the simultaneous action of the air and of caloric: and the well known necessity of not melting the ores does not seem to be recommended in consequence of the fear of communicating to it, together with liquidity, a force of cohesion which will oppose the separation of the sulphur; but rather because this state will confine the action of the air to a surface, which, not being capable of being renewed, will be soon covered by the metallic oxide. The combination of the oxygen with the elements of the sulphurets, gives birth to oxides and to acids, the affinities of which have great influence upon the separation of the sulphur, and the results of a roasting: the latter generally present a mixture of oxide, of sulphate, and of indecomposed sulphuret. I shall examine separately and in detail the roasting of several kinds of sulphurets, because the nature of the metal produces great modifications in their results; and shall presently show, why, and in what form, the sulphur is separated.

* Macquer, in this respect, agrees with the metallurgists. We find in his Dictionary of Chemistry the following passage: "There are several methods of separating sulphur from metallic substances: in the first place, as sulphur is volatile, and as these substances are fixed, or at least not so volatile as sulphur, the *action of heat alone is sufficient* to take the sulphur from most metals." He seems, however, to have been aware of the importance of the contact of the atmospheric air in roasting, since he says, when speaking of the sulphurets of mercury and of arsenic, "It will be possible to desulphurate them without intermedium, by a well-managed heat and *in the open air*."

Roasting of Pyritous Copper.

We arrange pieces of pyritous copper upon faggots, in such a way as to make the combustion continue a long time. The first application of the heat separates a part of the sulphur, which is distilled in some measure, and may be collected: but afterwards it is this combustible which serves, upon burning, to continue the operation: sulphurous acid is liberated, the elasticity of which, increased by the elevation of the temperature, hinders its combination with the metallic oxides. The sulphuric acid which is formed, in spite of the care taken to slacken the combustion, is united to the oxides of copper and iron, but the sulphate of iron is partly decomposed by the hyper-oxidation of the metal.

The pyrites of iron submitted to the same operation undergoes *analogous decompositions*, the succession of which is in every respect the same.

The roasting of pyritous copper in the reverberatory furnace produces the same phænomena, and seems as if it would admit of a much more complete separation of the sulphur, than that produced in the open air. If it were not so, it would no doubt be owing to the difficulty of hindering the agglutination of the sulphuret produced by the elevation of temperature, owing to the rapid and inevitable combustion of a great quantity of sulphur.

I come now to speak of a furnace, in which we effect at the same time both the melting and the roasting (to a certain degree) of pyritous copper: this is the method practised at Falhun in Sweden*, and is done with an inner crucible,

* We find the following observations in the *Voyages Métallurgiques*, by Jars, tome iii. pages 55 & seq. "The flux of the mineral roasted a single time, is effected in a furnace which has an inner bason destined to contain the produce of the operation."—"When it is heated, it is charged with a good deal of scoriæ from the flux of black copper, with quartz and a little mineral."—"They do not mix the quartz with the mineral, but only add it when there are any fears of mischief in the inner bason."—"The fusion of the roasted pieces (*mattes*) is effected in the same kind of furnace, but smaller."—"The substances must remain a longer time in the furnace, which must not be opened until the end of twice twenty-four hours. They then extract a very few rich *mattes*, but a very large pig of black copper."—"This method of melting the pyrites is certainly the only one that can

cible, which receives the produce of a flux of 24 or 48 hours, and in which a separation, or rather a combustion, of the sulphur takes place. The wind of the bellows passes over the surface with sufficient force for removing the scorix, and burning a part of the sulphur on the surface: the iron is thus oxidized, and quartz is added in order to vitrify it in proportion as the roasting goes on*. It is thus that we may explain the concentration of the metal, and the general result of the flux, which surprised M. Jars very much. This process is perhaps the only one in which, at the same time, the sulphur and iron are separated in any quantity.

The de-sulphuration of pyritous copper by roasting, is, in my opinion, produced, 1st, by the sublimation of a small portion of sulphur, which may be collected or burnt in the air: 2dly, by the extrication of sulphurous acid, so much the more abundant as the operation is well conducted †: 3dly, by the vaporization of a little sulphuric acid, the greatest part of which, however, remains united to the copper.

can be used, and which, in spite of the inconveniences it presents, may nevertheless be advantageous.”—“Another very precious advantage is a concentration of the metal contained in the fluid matter which is continually agitated by the wind of the bellows. They extract a smaller quantity of mattes, but they are richer. We confess our surprise at the flux of black copper, when we see the small quantity of rich mattes which comes from a very inferior sort of ore, and which does not even seem to have been roasted.” We should be of M. Jars’ opinion, that this method of melting pyritous copper is one of the best, if more copper was not volatilized than by the other processes: but if, as I think, we may substitute the reverberatory furnace for that used at Falhun, and in other respects following up the same series of operations, there would certainly be great advantages derived over fusion in the hand furnace.

* Swedenborg (*de cupro*) thus expresses himself: “*Plurima ejus ars* (meaning the melters) *in eo consistit, ut lapidem siliceum, justo tempore et modo, sciat offerre.*”

† Recent experiments of Messrs. Clements and Desormes show, that the combustion of sulphur does not produce sulphuric acid so easily as imagined: but we know that its formation is determined by various peculiar circumstances, such as the presence of the alkalis, oxides, &c.

[To be continued.]