UNITED STATES PATENT OFFICE.

ERASTUS L. STONER, OF SCOTTDALE, PENNSYLVANIA.

PROCESS OF DESULFURIZING COKE.

No. 887,145. Specification of Letters Patent. Patented May 12, 1908.

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To all whom it may concern:

Be it known that I, ERASTUS L. STONER, a citizen of the United States, residing at Scottdale, in the county of Westmoreland and State of Pennsylvania, have invented or discovered new and useful Improvements in Processes of Desulfurizing Coke, of which the following is a specification.

My invention relates to processes of eliminating sulfur from coke and its object is to improve the quality of coke by removing the sulfur to the desired limit by the use of reagents involving chlorin.

Sulfur in coal usually exists in the form of pyrites (FeS_2), gypsum or calcium sulfate ($CaSO_4$), or organic sulfur, which is sulfur combined with the carbon, hydrogen and oxygen of the coal.

It is my purpose in the present specification to deal only with pyrites as it exists in the coal and is transformed to other chemical forms by the coking processes, but it is to be understood that I do not waive the right to protection herein for all uses to which my claims may apply, whatever the character of the combinations with sulfur may be.

In the coke-burning processes now in use, one-half of the sulfur is, under very favorable circumstances, volatilized, if the organic sulfur is not present in excessive quantity. The sulfur expelled comes partly from that which is present in the form of organic compounds, but for the larger part form that which is present as pyrites, or di-sulfid of iron, the sulfur of which is given off, even at a low temperature, as sulfur vapor. The statement in regard to one-half of the sulfur being expelled by the usual coking processes is exemplified by the following chemical reaction:

$$7FeS_2 = Fe_7S_8 + 6S.$$

This reaction resolves itself for practical purposes into $FeS_2 = FeS + S$, that is, substantially one-half the original sulfur is burned off or volatilized if the sulfur is present as pyrites. The volatile matter enters here as an important factor, since with the usual percentage of volatile matter in coal, the sulfur in the coke is, owing to the loss in weight in the coking process increased from one-third to one-half, so that in reality only about one-fourth of the original per cent. of sulfur is eliminated in the ordinary method of coking.

The organic sulfur remains for the most part in the coke. A part of the volatile sulfur will also be retained by certain constituents of the ash, especially compounds of iron, such as the carbonate, oxid, and silicate, and also compounds of calcium and magnesium. These compounds of iron are reduced in the process of coking by compounds of carbon to the metallic condition, and this even at a low red heat. The reduced iron, by virtue of its powerful affinity for sulfur, combines with a part of the sulfur set free from the original pyrites (FeS_2) in the coal, to form iron sulfid (FeS).

The carbon compounds formed in the coke oven and containing sulfur, as carbon di-sulfid (CS_2) form sulfids with iron and with the red-hot oxids of the alkali metals. The sulfates present, especially gypsum ($CaSO_4$) are partially reduced to sulfids in the oven.

My process is based on the law that all sulfids are decomposed more or less readily by hydrochloric acid gas (HCl), hydrogen sulfid (H_2S) and a chlorid being produced, and in some cases sulfur being also eliminated, and consists in chlorinating the coke preferably at or near the completion of the coking process. This process is greatly facilitated if the sulfids are at a red heat such as is usually found in the ovens at the close of the coking process, or after the volatile matter has been practically driven off. The law above stated may be illustrated by the chemical equations in which some of the sulfids that form a part of the coke are used, for example:

$$FeS + 2HCl = FeCl_2 + H_2S$$
$$CaS + 2HCl = CaCl_2 + H_2S$$
$$Na_2S + 2HCl = 2NaCl + H_2S$$
$$K_2S + 2HCl = 2KCl + H_2S.$$

From these formulæ, it is seen that the sulfids of the coke are converted to volatile and soluble chlorids while the sulfur passes off as hydrogen sulfid, which may later be subjected to an oxidizing influence. The remaining soluble chlorin salts may be washed from the coke by the usual "watering out" processes.

Chlorin gas forms the basis of my process for reducing the sulfur in the coke. This gas may be generated in any manner that best suits the circumstances. The chlorin gas is preferably passed into superheated steam

and then the resulting gases are applied to the coke in the ovens. These gases are expressed by the following chemical reaction:

$$2H_2O + 2Cl_2 = 4HCl + O_2.$$

In my process it is definitely understood that the chlorin gas and superheated steam must be transmitted through a chamber heated to bright redness and then the resulting mixed gases of HCl and O, while still in a highly heated condition, are applied to the coke.

In my process it is essential that both the mixed gases be in a highly heated condition and the coke red-hot, for a two-fold purpose; first, that the various sulfids, which must be in such condition as has been enunciated in the chemical law hereinbefore laid down, may be readily decomposed by the HCl gas: secondly, that the application of the gases may have no "quenching" effect upon the coke, since it is not the purpose of the process to "quench" the coke by means of the gaseous HCl and O. Such an arrangement would stultify and be diametrically opposed to the underlying principle of the process; namely, a red-hot condition of all sulfids for a successful reduction thereof.

In addition to the above chemical and physical laws of the process, I wish to point out one other important factor. It will be noted that it is a mixture of superheated gases that is supplied to the red-hot coke, which is composed of HCl and O. The action of the HCl gas has been described and forms the primary feature of the process. The secondary chemical element is the free O and its action upon the various compounds in the coke. The free O gas, acting meritoriously, may partly oxidize the sulfids of the coke to oxids of the respective elements thus freeing the sulfur as an oxid, or it may oxidize the H_2S to water and an oxid of sulfur; and, acting deleteriously, the free O gas may destroy a certain part of the carbon of the coke.

I do not wish to restrict myself to any of the above reactions for free O. It may react in any one and in all of the above prescribed ways and in other ways not described in the process.

By the above minutiæ of the process, I claim a new process for desulfurizing coke, differing materially from any process now extant.

I do not restrict myself to any method of applying the chlorinating gases to the coke. It may be passed through the same from the bottom or sides or both, or from the top.

I do not restrict myself to the precise compounds with chlorin although I have mentioned the use of hydrochloric acid gas.

The strength of the hydrochloric acid may be varied in any desired way, as by varying the amount of steam used with the chlorin.

I claim—

1. The process of treating coke made from coal containing sulfids, which consists in subjecting the coke to the action of a chlorinating gas at the close of the coking process and then watering out the fire and thereby washing out the remaining soluble salts.

2. The process of treating coke made from coal containing sulfids, which consists in subjecting the coke at the close of the burning process to highly heated chlorinating gases and then watering out the fire and thereby washing out the remaining soluble salts.

Signed at Pittsburg, Pa., this 7th day of November, 1907.

ERASTUS L. STONER.

Witnesses:

ALICE E. DUFF

F. N. BARBER.