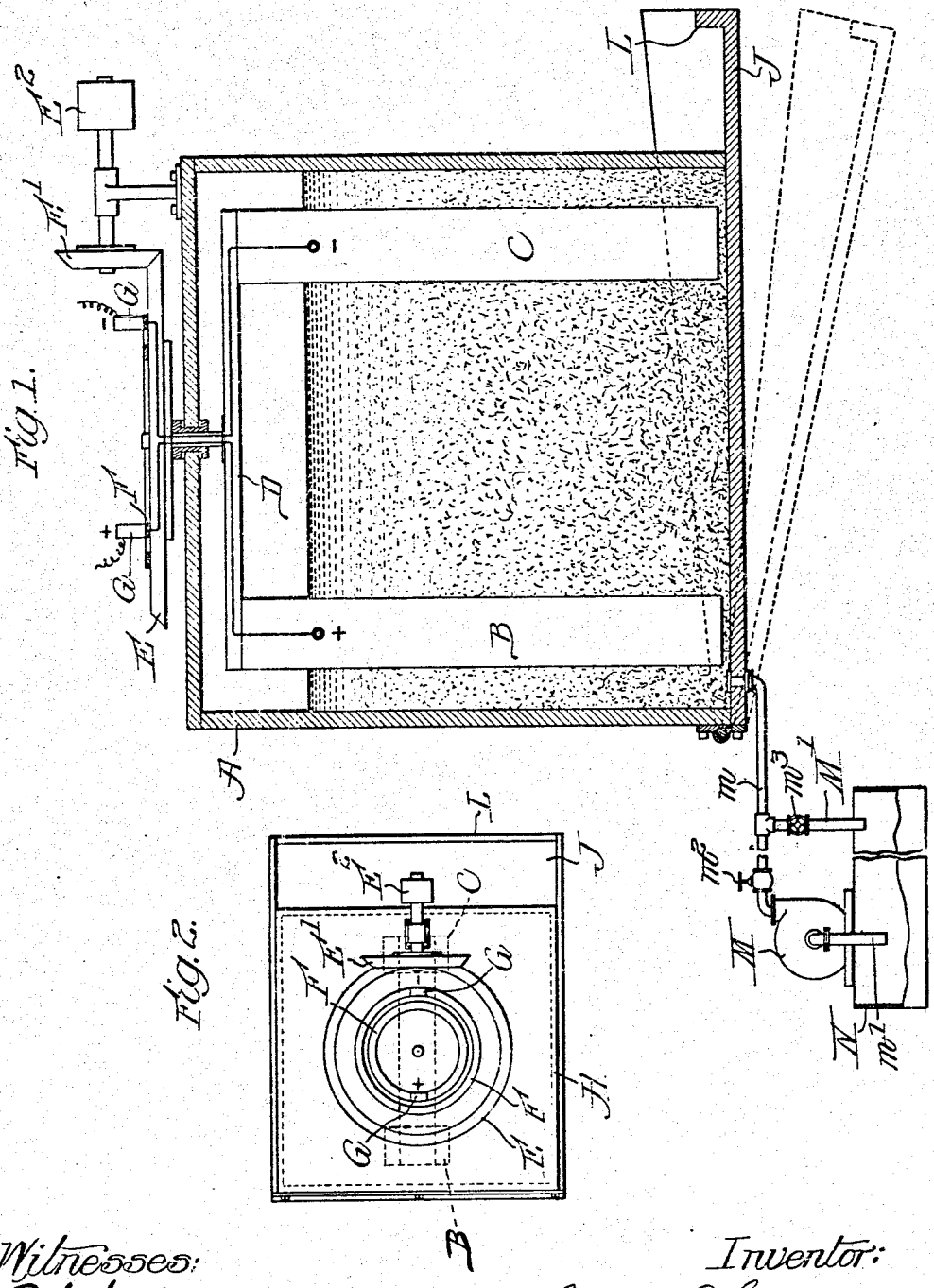
L. L. SUMMERS.

METHOD OF EXTRACTING OR ELIMINATING SULFUR, PHOSPHORUS, AND OTHER IMPURITIES FROM COAL, ORE, &c.

APPLICATION FILED APR. 8, 1909.

967,996. Patented Aug. 23, 1910.

2 SHEETS—SHEET 1.



Witnesses:
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Harold G. Barrett.

Inventor:
Leland L. Summers
By Rector, Hibben & Davis
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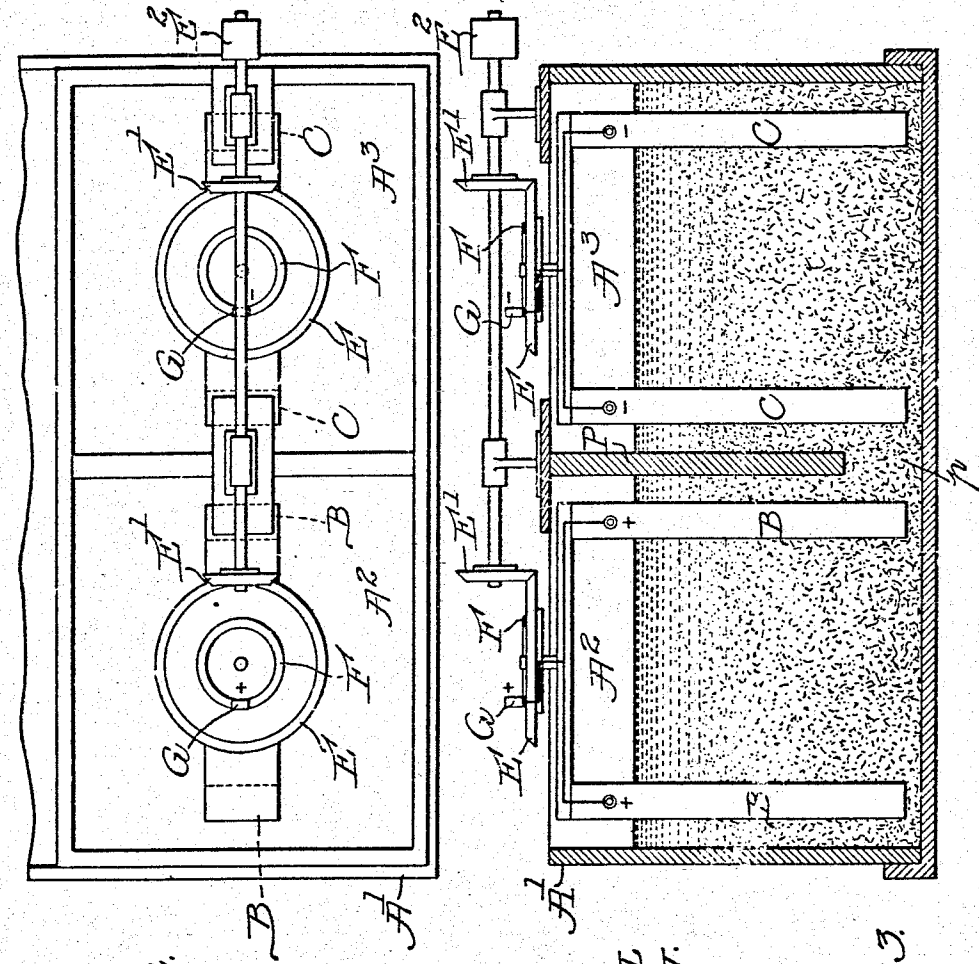

Fig. 4.

Fig. 3.

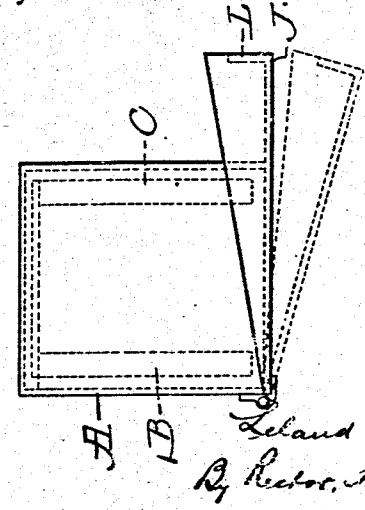

Fig. 5.

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UNITED STATES PATENT OFFICE.

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METHOD OF EXTRACTING OR ELIMINATING SULFUR, PHOSPHORUS, AND OTHER IMPURITIES FROM COAL, ORE, &c.

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To all whom it may concern:

Be it known that I, LELAND L. SUMMERS, a citizen of the United States, residing at Chicago, Cook county, Illinois, have invented certain new and useful Methods of Extracting or Eliminating Sulfur, Phosphorus, and other Impurities from Coal, Ore, &c., of which the following is a specification.

My invention relates to a method of extracting or eliminating those impurities from coal ore, etc., which are both detrimental and troublesome in the manufacture of iron and steel, and the object is to provide a simple and efficient method of removing such impurities from the raw material used. Thus, according to my method, in the case of coal to be coked the sulfur and phosphorus are removed from the coal before the same is charged into the coking appliances, and in the case of ore, the impurities are removed previous to charging the ore into the blast furnaces or other refining apparatus.

In general terms, my invention consists in providing a method by which the sulfur and phosphorus is chemically acted upon and its form of occurrence changed so that it may be removed as a different chemical compound. Sulfur and phosphorus in coal are very detrimental to its use as a fuel for metallurgical purposes. The sulfur in the coal exists in a number of different forms, part of the sulfur being combined in the coal in such manner as to pass off in a volatile form when the coal is coked or strongly heated. Another portion of the sulfur is combined with foreign matters in the coal, so that it may be eradicated previous to coking the coal. That portion of the sulfur combined in the coal and which forms a volatile constituent upon heating, does not exert a deleterious effect, as it does not remain in the coke. However, the portion of the sulfur combined with iron and other matters is very difficult to remove, as upon heating the coal in a coke oven or furnace with a limited supply of air or oxygen the reducing atmosphere necessarily existing effectually prevents removal of the sulfur.

As the general characteristics of phosphorus resemble those of sulfur in forming phosphids and phosphates as sulfur forms sulfids and sulfates, the treatment for removing the sulfur will ordinarily result in the removal of phosphorus. Hence, in this specification the details covering the one will in general apply to the other.

As sulfur exists in much greater quantities than phosphorus in coal, the following detailed explanation will be made in connection with the removal and treatment of sulfur, although the method is equally applicable to the removal and treatment of the phosphorus. Moreover, while for convenience I will describe my invention in connection with an apparatus suitable for the practice of such invention or method, yet it is to be understood that my invention is not limited, in respect to the method, to any character of apparatus but that my method may be practiced in other ways. Furthermore, I contemplate using my invention wherever applicable.

In the drawings, Figure 1 is a vertical sectional elevation of an apparatus suitable for the practice of my invention; Fig. 2 a plan view of such apparatus but on a smaller scale; Fig. 3 a vertical sectional elevation of a modified form of apparatus; Fig. 4 a plan view thereof; and Fig. 5 a detail elevation of the apparatus showing discharging means thereof.

Referring to the drawings, an electrolytic tank A of any suitable shape and dimensions is provided with revolving electrodes B and C mounted on an arm D and driven in any desired manner as by the gears E and E′ and pulley E^2 which, in turn are driven by any suitable source of power (not shown). The electrode D is connected to the positive wire from a suitable source of electrical energy through the contact ring F and brush G, and the electrode C is connected with the negative lead from the same source of electrical energy through said contact ring and brush.

The electrolytic tank of Figs. 1 and 2 has a single compartment in which the electrodes of different polarity revolve but if desired a double compartment tank may be employed as shown in Figs. 3 and 4 with electrodes of the same polarity revolving in the same compartment. In this form of apparatus, the tank A′ is divided into two compartments, A^2 and A^3 by the partition P which, however, permits of inter-communication between said compartments at *p*. The electrodes are driven in the same gen-

eral manner as those already described, but in this instance the electrodes B in compartment A^2 are of the same polarity (+), while those in the other compartment A^3 are of the opposite polarity (−). The electrodes B being in one compartment and the electrodes C in a separate compartment, the products of electrolysis are thus separated as is well known in the art.

My method is based essentially upon the well-known fact that upon the passage of an electric current in a suitable electrolyte, electrolytic decomposition will result. According to my method as practiced, the coal or ore to be electrolyzed is preferably in a finely subdivided form and is submerged in the electrolyte, so that upon revolving the electrodes B and C a continual agitation of the substance in contact with the products of electrolysis results. The electrolyte used may be varied to suit the character of the impurities existing in the ore or coal, the general action being as follows: A portion of the sulfur exists ordinarily in the form of the iron pyrites or bisulfid of iron FeS_2. Another portion of the sulfur exists as the monosulfid of iron FeS, and still another portion exists as the sesquisulfid Fe_2S_3. The monosulfid is readily decomposed by dilute mineral acids with the evolution of hydrogen sulfid and a salt of the metal, in accordance with the following equations:

$$FeS+H_2SO_4aq=FeSO_4aq+H_2S$$
$$FeS+_2HCL\ aq=FeCL_2aq+H_2S$$
$$FeS+_2HNO_3aq=Fe(NO_3)_2aq+H_2S.$$

The monosulfid of iron is not readily oxidized. The bisulfid of iron FeS_2 resists the action of mineral acids, but may be oxidized (in the presence of moisture) to the ferrous sulfate $FeSO_4$ and the ferric sulfate $Fe_2(SO_4)_3$. The sesqui-sulfid of iron is partially converted into the one and partially into the other form by oxidation and by dilute acids. The action of oxygen and water on the bisulfid is expressed by the following equation:

$$FeS_2+3O+H_2O=FeSO_4+H_2S.$$

In my method of extracting the sulfur I preferably use an acid or acid-forming electrolyte such as sulfuric acid in water or any soluble sulfate which will have a combined decomposing action on the sulfids of iron, the acids converting the monosulfid into hydrogen disulfid and a soluble sulfate, at the same time that oxygen and water are decomposing the bisulfid.

As the electrolyte is decomposed by the electric current, the acid radical and the oxygen traveling to the positive pole or anode causes an active and effective action on the substances in the vicinity of the anode. Thus, the particles of FeS_2 are oxidized in the electrolyte, the product being soluble ferrous and ferric sulfate and hydrogen sulfid, while the monosulfid of iron is acted on by the acid.

The hydrogen sulfid formed by the above reactions is decomposed by the oxygen, in accordance with the following equation:

$$H_2S+OH_2O+S.$$

The product of this action is thus water and free sulfur. The sulfur thus existing is inert to the acid and is but slowly oxidized by the oxygen. In this form the electrolytic action could be discontinued and the coal then treated separately with a solvent for sulfur such as benzol C_6H_6 or ethyl-alcohol C_2H_6O or electrolytically or otherwise with a solvent such as sodium hydroxid NaOH. If treated with a solution of sodium hydroxid the sulfur will be placed in solution in the form of sulfids and thiosulfates of sodium. Thus,

$$4S+6NaOH=2Na_2S+Na_2S_2O_3+3H_2O.$$

If desired the acid electrolyte may be drained from the tank or cell and an electrolyte of sodium hydroxid then placed therein and the electrolytic action continued, with the result that the sulfur will thus be acted on by the sodium hydroxid, which will be in an active electrolytic form. The alkaline solution taking the place of the acid solution will further act on the soluble sulfates forming the iron hydrates. If an acid salt, precipitated by hydrogen sulfid be used, such as copper sulfate or a lead salt, it will be possible to have the sulfur deposited by the action of the hydrogen sulfid in the presence of these metallic salts decompose the metallic salt and form a metallic sulfid which may be caused to have a sufficient specific gravity so that the agitation from the revolving electrodes will cause these sulfids to sink to the bottom of the cell and be readily separated from the balance of the material treated. If the electrolyte used is such that the presence of hydrogen sulfid may be caused to form a soluble sulfid such as will be the case when zinc sulfate is used, the deposited sulfur may be eliminated as a soluble sulfid. The quality of the coal and the form in which the sulfur is obtained will ordinarily determine definitely which electrolyte to use.

In the above reaction, the electrodes B and C are assumed to be of carbon, platinum or other material not affected by the electrolytic action. If, however, a metal electrode such as copper is used in an acid electrolyte such as H_2SO_4 the metal will be dissolved in the electrolyte and can be caused to unite with a portion of the sulfur as either soluble or non-soluble sulfates and sulfids depending on the metal used and the intensity of the reaction.

In ordinary practice with the Illinois coals

I prefer to use as an electrolyte a neutral salt of the alkali metals, such as sodium sulfate or sodium nitrate. In an electrolyte composed of 10% to 15% of normal sodium sulfate in a solution of water, the electrolytic decomposition will result in the acid radical SO_3 and oxygen being liberated at the anode and the metal sodium at the cathode. The metal sodium immediately enters into a secondary reaction by which the sodium decomposes the water of the electrolyte, the products being hydrogen and sodium hydroxid. The action will thus be to cause an acid reaction in the vicinity of the anode and an alkaline reaction in the vicinity of the cathode. By the reversal of the current or the reversal of the electrodes by revolving or otherwise agitating either the solution or the electrodes, this action may be reversed at will, that is, one portion of the electrolyte will be subjected to an acid and oxidizing influence, the other portion of the electrolyte being submitted to an alkaline and a reducing action from the liberated hydrogen, the activity and strength of these reactions being controlled by the current density and the length of time the electrode remains in contact with the substance.

In the apparatus of Fig. 1 the rotation of the electrodes B and C in addition to agitating the electrolyte will cause a portion of the material treated to first be subjected to the acid and oxidizing reaction and immediately afterward to be subjected to the alkaline and reducing action. Thus, the bisulfid and monosulfid of iron in the vicinity of the anode will be violently reacted upon, the bisulfid being oxidized and the monosulfid being decomposed as before mentioned. Immediately after this action, the same particles will be subjected to the action of the sodium hydroxid liberated by the cathode, this being caused by the rotation of the electrodes so that the cathode and anode are changing places. The rate of rotation is determined by the strength of the reaction desired.

In the apparatus of Fig. 3 the anode and the cathode occupy separate compartments, the passage of the current causing the acid and oxidizing reaction to take place in the compartment A^2 connected to the positive pole and an alkaline and reducing reaction taking place in the compartment A^3 connected to the negative pole. The agitation of the electrolyte in the revolving of both electrodes causes each particle to be subjected for a considerable time to the desired reaction. The current is then reversed, causing the compartment in which the acid and oxidizing reaction has been taking place to be connected to the negative pole and the compartment in which the alkaline and reducing action has been taking place to be connected to the positive pole, the effect being to reverse the reactions and the compounds formed in the two compartments will therefore be reversed. In this way the sulfur formed in the decomposition of the hydrogen sulfid and the pyrites is absorbed by the alkali formed at the cathode. At each reversal of the current in the case of Fig. 3 or at each rotation of the electrode in the case of Fig. 1 a definite reaction is caused to take place. The tendency to change from an acid to an alkaline condition or vice-versa immediately acts upon the compounds of sulfur which have been formed in the previous condition of reaction, the general tendency being to oxidize the sulfur into a soluble sulfate. In this way the chemical activity is constantly preserved and at the same time the violence of the reaction can be easily controlled, so that a substance easily acted upon such as coal will not suffer decomposition by the use of violently acting reagents. Thus, the use of a normal salt in the treatment of many coals possesses a distinct advantage, as the coking action of a coal is greatly affected by both oxidizing or reducing actions if they are too strongly applied.

In decomposing a salt such as sodium sulfate into an alkaline and an acid radical, as above described, the sodium sulfate will be regenerated from the soluble sulfates when the alkaline reaction forms the iron hydrates as follows:

$$FeSO_4+2NaOHaq=Fe(OH)x+Na_2SO_4aq.$$

In treating iron ores this reaction will precipitate the sulfates acted upon in the form of pure ore as the hydrates decompose into the oxids, or most common form of iron ore, and sodium sulfate is thus restored to the solution.

It will be apparent from the above description that I do not confine myself to the use of any one electrolyte, as the current densities used will permit the use of many acids or salts of acids and alkalis. In the treatment of many substances for the elimination of sulfur, it is undesirable to use a compound of sulfur and, hence, the acid reaction may be obtained by hydrochloric, nitric or other acids and the alkaline action or the solvent action obtained by other alkalies such as ammonia or by solvents for sulfur. Thus, the sodium nitrate or ammonium nitrate can be electrolyzed and an acid reaction due to the acid radical obtained, and the alkaline reaction simultaneously obtained from the alkali liberated at the cathode.

The time required and the current densities necessary for producing the reactions above outlined will depend in a measure upon the electrolyte used and also upon the particular coal or ore treated. In general

a current density of from two to three amperes per square inch of electrode will produce satisfactory results in from three to five hours, depending on the amount of impurities to be removed.

In the side elevation, Figs. 1 and 5, the bottom J of the electrolytic cell is shown provided with a lateral extension or projection L, the action being that when the bottom of the cell is swung downwardly on its hinge and thereby dropped for discharging the material, the material in the cell A is discharged along the bottom, which forms a chute or sluice. The projection L, however, acting as a riffle, withholds that portion of the material which was deposited at the bottom of the cell, and causes the portion of the material in the upper parts of the cell to be freely discharged over the top of the projection L. A number of these projections or riffles L may be formed, if desired, the object being to cause the lower portion of the material treated to be held back and discharged into a separate compartment from that contained in the upper portion. In the treatment of coal, constant agitation in the aqueous electrolyte will cause the heavier particles of slate, silica, and mineral impurities to sink to the bottom of the cell. By means of the riffle L, the material in the lower portion of the cell is readily separated without further action. In this manner the electrodes B and C may be used to cause a chemical reaction and precipitate portions of the sulfur or other impurities in a chemically combined form that will sink to the bottom of the cell while other portions of the impurities are being taken up in the manner above described, and in this way a combination of the methods may be utilized in one cell.

For convenient and rapid operation in supplying the tank with the electrolyte and draining the same therefrom and the substitution of other electrolyte as hereinbefore referred to, suitable mechanical means may be provided, as for instance the pump arrangement more or less diagrammatically shown in Fig. 1 where a centrifugal pump M is shown connected to the bottom of the tank with a discharge pipe m and provided also with a suction pipe m' which extends into a source of electrolyte within a suitable container such as the tank N. In order that the electrolyte may be drained back into the same tank or into some other tank if two characters of electrolyte are used, I provide the discharge pipe m with a branch pipe M' and provide such pipe with suitable shut-off valves m^2 m^3 all as clearly indicated in Fig. 1, suitable provision being of course provided to permit of the swinging bottom J of the tank in the manner already explained.

Having thus described my invention, I claim:

1. The method of eliminating phosphorus or sulfur from coal ore, or the like, which consists in subjecting the material containing such substance or substances to electrolytic action by which an oxidizing and acid reaction is simultaneously produced.

2. The method of eliminating sulfur and phosphorus from coal ore or the like which consists in subjecting the material containing such substance or substances to an electrolytic treatment by which the material is subjected to a combined acidifying and oxidizing reaction and then removing the secondary products by the action of suitable solvents.

3. The method of eliminating sulfur or phosphorus from coal ore, or the like, which consists in alternately subjecting the material to an acidifying and oxidizing influence and a reducing and alkaline influence.

4. The method of eliminating sulfur or phosphorus from coal, ore or the like, which consists in subjecting the material containing such substance or substances to electrolytic action, the electrolyte containing a solvent for the products resulting from such action.

5. The method of eliminating sulfur or phosphorus from coal, ore or the like, which consists in subjecting the material containing such substance or substances to an acidifying and oxidizing reaction in an electrolyte in which the products resulting from the reaction are soluble.

6. The method of eliminating sulfur or phosphorus from coal, ore or the like which consists in subjecting the material to an acidifying and oxidizing influence and taking up the products of the reaction in a liquid solvent.

7. The method of eliminating sulfur or phosphorus from coal, ore or the like which consists in treating the material in a finely divided condition with a solution capable of acting upon the sulfur or phosphorus, causing the products of the reaction to be taken up.

8. The method of eliminating sulfur or phosphorus from coal, ore or the like which consists in treating the sulfur or phosphorus to be removed alternately with solutions capable of forming compounds of sulfur or phosphorus and of oxidizing the sulfur or phosphorus into soluble compounds.

9. The method of eliminating sulfur from coal and the like, which consists in submerging the substance to be acted upon in a suitable electrolyte, and then alternately subjecting the substance to the action of electrodes of opposite polarity.

10. The method of eliminating sulfur from coal and the like, which consists in

submerging the substance to be acted upon in a suitable electrolyte, and then alternately subjecting the substance to the action of electrodes of opposite polarity by changing the position of the electrodes with relation to the substance.

11. The method of treating coal containing sulfur or sulfur compounds which consists in electrically treating the coal and then further treating the said coal by suitable chemical re-agents to remove the sulfur.

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