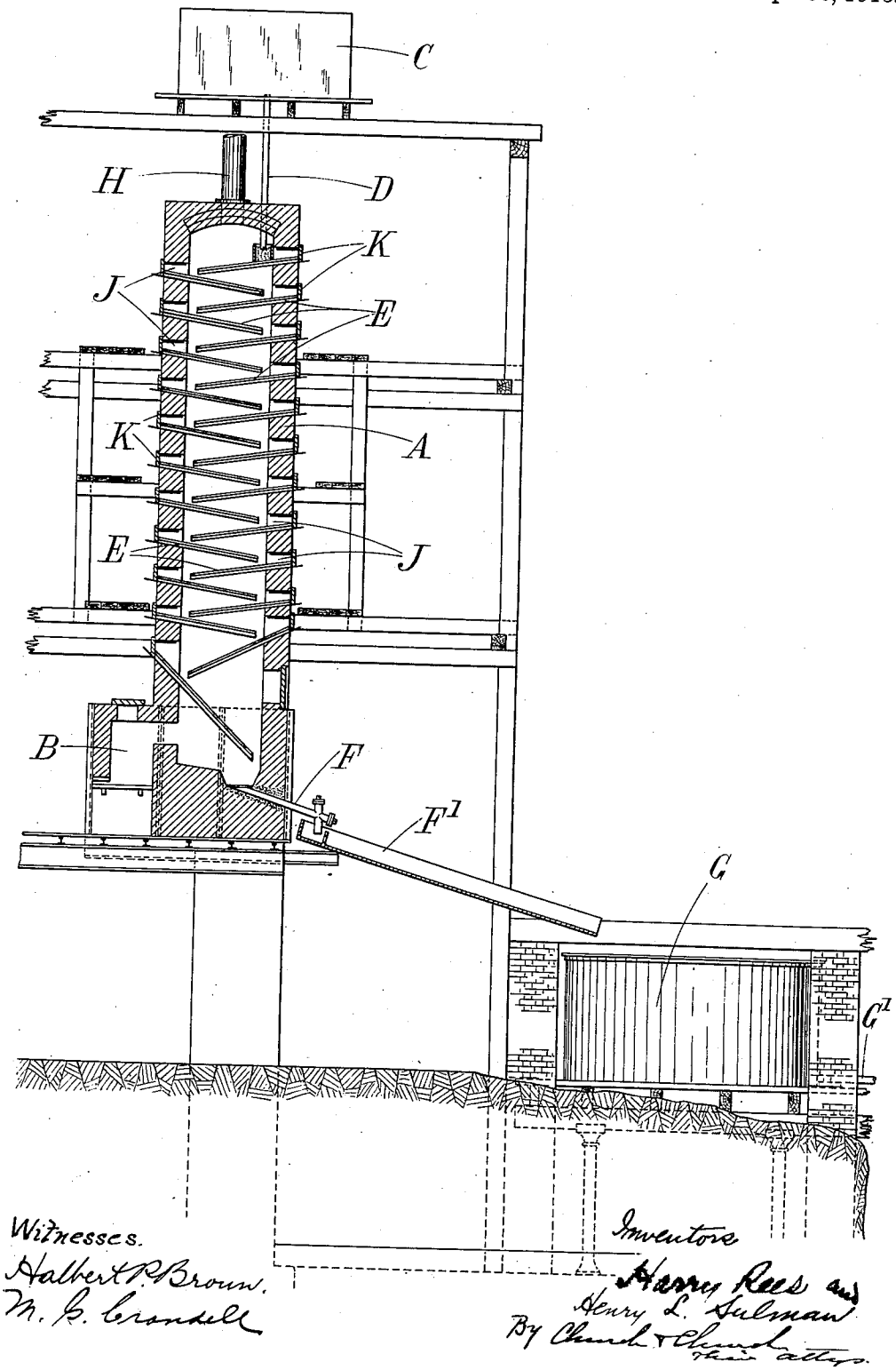
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DEPOSITION OF METALLIC SALTS FROM SOLUTIONS CONTAINING THEM.

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DEPOSITION OF METALLIC SALTS FROM SOLUTIONS CONTAINING THEM.

1,074,203. Specification of Letters Patent. Patented Sept. 30, 1913.

Application filed August 18, 1911. Serial No. 644,798.

To all whom it may concern:

Be it known that we, HARRY REES and HENRY LIVINGSTONE SULMAN, subjects of the King of England, residing at Llansamlet, Glamorgan, Wales, and London, England, respectively, have invented certain new and useful Improvements in the Deposition of Metallic Salts from Solutions Containing Them, of which the following is a specification.

This invention relates to improvements in the deposition of metallic salts from solutions containing them and has for its object the recovery of certain metallic salts from solution by heating the latter under conditions hereinafter described, such salts being thereby obtained in an insoluble form, and in a more basic condition than that in which they existed when dissolved.

The invention can be applied to the recovery of salts of copper, zinc, etc., but is especially applicable to solutions of bisulfite and sulfate of copper or zinc, such as those resulting from the treatment of roasted simple or complex ores of copper or zinc with aqueous sulfurous acid which may, or may not contain free sulfurous acid in addition thereto. Dealing with zinc for example, if such solutions are heated to a temperature of, say, 80° C., while in mass or bulk, they undergo little or no change, unless the period can be prolonged, when some sulfur dioxid is expelled from solution and a small amount of zinc monosulfite may form as a scum on the surface or fall as a slight precipitate, not however in a basic condition; while the sulfate of zinc contained therein remains quite unaffected and soluble. If, however, such solutions be exposed in films in a heating apparatus such for preference as that hereinafter to be described, *i. e.* if a continuous current of liquor be made to flow filmwise over a series of plates or shelves heated either externally, or internally by the gaseous products of fuel combustion, the zinc salts are deposited from the solution more or less completely, frequently in a more basic condition; thereafter remaining insoluble in the liquor. These reactions take place though the temperature of the liquor finally escaping from the apparatus may not exceed 80–90° C. The separation of the metallic salts described is not effected by decrease in the bulk of the liquor due to evaporation, but sulfur dioxid resulting from the decomposition of the bisulfite and possibly of some monosulfite, escapes with the cooled inert gases from the apparatus.

According to this invention a process for depositing salts of the kinds described from a solution containing them consists in forming a continuously moving thin film of the solution and subjecting it to the action of heat.

According to the preferred method of carrying the invention into effect the thin film of the solution is passed over a heated surface or is passed in cascade over a number of heated surfaces and in contact with an ascending heated atmosphere.

Apparatus for carrying out the process, comprises a chamber accommodating several shelves arranged in cascade formation, a source of heat and a connection delivering the hot fuel gases underneath the lowermost shelf.

In the accompanying drawing there is illustrated in sectional elevation one form of apparatus for carrying out the present invention.

Referring to the drawing, a shelf tower A is employed heated internally by the products of fuel combustion from the furnace B. The liquor containing the zinc salts to be recovered (for example the solution of zinc bisulfite) is contained in a tank C, from which it is fed to the top of the tower through the pipe D. The liquor is allowed to flow downward through the tower in thin sheets or films, over a series of downwardly inclined shelves E arranged to project alternately from opposite sides of the tower to give a zigzag passage to the liquors which finally escape at the bottom of the tower through the conduit F and the conduit F′ to the collecting tank G.

The tank is preferably provided with a draw-off pipe G′. Hot gases from the coke or other suitably fired stove B pass upward through the openings between the shelves in an opposite direction to the flow of the liquors and heat the lower shelves to a considerable degree upon their under sides. The tower is made however, of such height that the inert combustion gases which are without chemical action upon the liquors are

almost completely cooled before they escape at the top of the apparatus through the chimney H. The tower may be constructed of refractory brick, slabs or other suitable material capable of resisting the action of acid liquors or gas. The heat is thus applied with great economy and efficiency, as the combustion gases are made to impart practically all their heat to the liquor and the metallic salts derived therefrom.

The shelves are preferably constructed of metal plates having at each side a low wall formed of channel iron to prevent the liquor from flowing over the sides of the plate. Openings J are provided in the walls of the tower A for the insertion and removal of the plates and these opening may be covered in any suitable manner to prevent the gases escaping from the tower. For example, they may be covered by hinged doors K on the outside of the tower. The pipe D from the tank C after passing into the tower dips into a small vessel of the liquor, thereby forming a seal so that the gases do not enter the pipe D.

A heat-exchange apparatus may be suitably arranged with regard to the hot outflowing liquors by which these are caused to impart their heat to the cold inflowing liquors which it is sought to precipitate; thus permitting of a saving in the coke used. Such an apparatus has previously been used for the evaporation and concentration of aqueous liquids and acids. In the present the issuing liquors are under 100° C. in temperature, and any small amount of local evaporation taking place in the lower portions of the tower are mainly condensed in the upper portions thereof, and returned with the downflowing liquor.

Sulfur dioxid is evolved from the liquors as before stated, and after the saturation limit of the colder inlet liquors by sulfur dioxid is reached the excess of this gas continually evolved in the lower portion of the towers, escapes with the cooled combustion gases, and may thereafter be utilized if desired. No claim is made *per se* to this method of eliminating the sulfur dioxid from aqueous solutions, as it has been employed, in principle, in the concentration of aqueous sulfurous acid. Under these conditions the behavior of such solutions is quite different from that of the same solutions when heated in bulk to the same temperature as that of the liquors finally issuing from the tower. Thus it has been found that monosulfite of zinc is readily separated from the films of liquid thus treated, and that in some cases it is partially decomposed into zinc oxid with loss of sulfur dioxid; further, that zinc sulfate is also to a small extent rendered insoluble possibly being converted by inter-action with the zinc oxid, into a basic sulfate of zinc. There are several basic sulfates of zinc known which have been isolated such as tetrabasic salt, $ZnSO_4 7ZnO$, hexbasic salt, $ZnSO_4 5ZnO$, and octobasic salt, $ZnSO_4 7ZNO$. A basic sulfate of zinc may be produced by heating the normal sulfate of zinc until it is partially decomposed and it is possible that some small proportion of zinc is formed in this way on the hottest portion of the shelf plates; the major portion however, is produced by the action of the sulfate of zinc liquors upon zinc oxid arising from the decomposition of the zinc sulfite, these joint reactions occurring on the shelves of the precipitation tower. These separated solids partially escape in the solution issuing from the apparatus, and partially remain as film accretions on the inclined plates or shelves, from which they may be removed periodically by scraping; suitable gas-tight doors being provided in the sides of the towers to allow this to be effected.

The solutions employed in the process are dilute and the precipitation of the zinc sulfate therefrom depends to a certain extent upon the proportion of bisulfite which is precipitated from the solution as monosulfite. The zinc sulfate would not precipitate by itself but requires the precipitation of the monosulfite or oxid to bring any zinc sulfate out of solution.

With a highly sulfated roast there might not be sufficient monosulfite to effect the precipitation of any zinc sulfate, but according to a modification of this invention this deficiency can be made good by adding to the dilute solution a sufficiency of either zinc oxid or zinc monosulfite. These additions are made to the solution before it is exposed filmwise on the shelves of the heated tower or the solution may be subsequently agitated for a short time with these reagents at a temperature of about 80° to 90° C. The result is that the zinc as bisulfite in the solution is precipitated as monosulfite and this together with the added monosulfite or zinc oxid or both secures the precipitation of some of the zinc sulfate in admixture therewith and in a basic condition.

In the particular apparatus described, the bottom slabs or shelves of the tower, *i. e.* those nearest to the stove, may be heated to a comparatively high temperature, as for example from 300 to 800° C., or even more; here the largest and most basic accretions form. This, however, does not communicate the same degree of temperature to the liquor films passing over them, for, as previously stated, the liquors escaping from the tower are as a whole heated to a temperature of less than 100° C. By increasing the height of the tower and the heat imparted to the liquors by means of the stove gases, increasingly basic precipitates may be obtained.

The following dimensions and quantities may be taken as a practical embodiment of the tower type of apparatus: Height of tower 13 ft. Cross-sectional area of the tower 21″x21″. Number of shelves—19 (the lower three shelves being composed of refractory material, such as fire-tiles). Inclination of all except the bottom shelf from the horizontal—10°. Inclination of bottom shelf from the horizontal 45°. Area of each shelf—2.77 sq. ft. (21″x19″). Size of coke grate—4 sq. ft. Volume of liquor passing through apparatus in 24 hours—50 short tons. Temperature of lowermost shelf on its under side approximately 800° C. Cross-sectional area of gas-way at constricted portions opposite the bottom edge of each shaft 0.44 sq. ft. (the area of the gas-way, however, varies at different points of its length).

It is obvious that the invention is not confined merely to the type of apparatus herein described, but any equivalent apparatus may be employed which will reproduce the conditions herein indicated and give the desired effect.

What we claim as our invention and desire to secure by Letters Patent is:—

1. A process for depositing monosulfite and sulfate of a metal from a solution containing bisulfite and sulfate of the metal, which consists in subjecting a continuously moving thin film of the solution to the action of hot gases from a coke fire.

2. A process for depositing monosulfite and sulfate of a metal from a solution containing bisulfite and sulfate of the metal, which consists in forming a continuously moving thin film of the solution, passing it over a heated surface and submitting it to the action of hot gases from a coke fire.

3. A process for depositing monosulfite and sulfate of a metal from a solution containing bisulfite and sulfate of the metal, which consists in forming a continuously moving thin film of the solution, passing it over a number of heated surfaces in cascade and submitting it to the action of hot gases from a coke fire.

4. A process for depositing monosulfite and sulfate of a metal from a solution containing bisulfite and sulfate of the metal, which consists in forming a continuously moving thin film of the solution and submitting it to the action of hot gases from a coke fire under a gradually increasing temperature.

5. A process for treating complex sulfid ores for the extraction of metal therefrom which consists in forming a solution of bisulfite and sulfate of the metal making up the deficiency of monosulfite salt required to effect the precipitation of the sulfate salt by adding to the dilute solution a sufficiency of an oxid thereafter depositing monosulfite and sulfate of the metal from the solution in an insoluble and basic form by subjecting a continuously moving thin film of the solution to the action of hot gases from a coke fire.

6. A process for depositing monosulfite and sulfate of zinc from a solution containing bisulfite and sulfate of zinc, which consists in subjecting a continuously moving thin film of the solution to the action of hot gases from a coke fire.

7. A process for depositing monosulfite and sulfate of zinc from a solution containing bisulfite and sulfate of zinc, which consists in forming a continuously moving thin film of the solution, passing it over a number of heated surfaces in cascade and submitting it to the action of hot gases from a coke fire.

8. A process for treating complex sulfid ores for the extraction of zinc therefrom, which consists in forming a solution of bisulfite and sulfate of zinc making up the deficiency of zinc monosulfite required to effect the precipitation of zinc sulfate by adding to the dilute solution a sufficiency of zinc oxid thereafter depositing monosulfite and sulfate of the zinc from the solution in an insoluble and basic form by forming a continuously moving thin film of the solution, passing it over a number of heated surfaces in cascade and submitting it to the action of hot gases from a coke fire.

In testimony whereof we have signed our names to this specification in the presence of the subscribing witnesses.

HARRY REES.
HENRY LIVINGSTONE SULMAN.

Witnesses to the signature of Harry Rees:
H. B. POYNDER,
B. THOMAS WERNELLYN.

Witnesses to the signature of Henry Livingstone Sulman:
FREDERICK READ,
WILLIAM GEORGE SELLERS.