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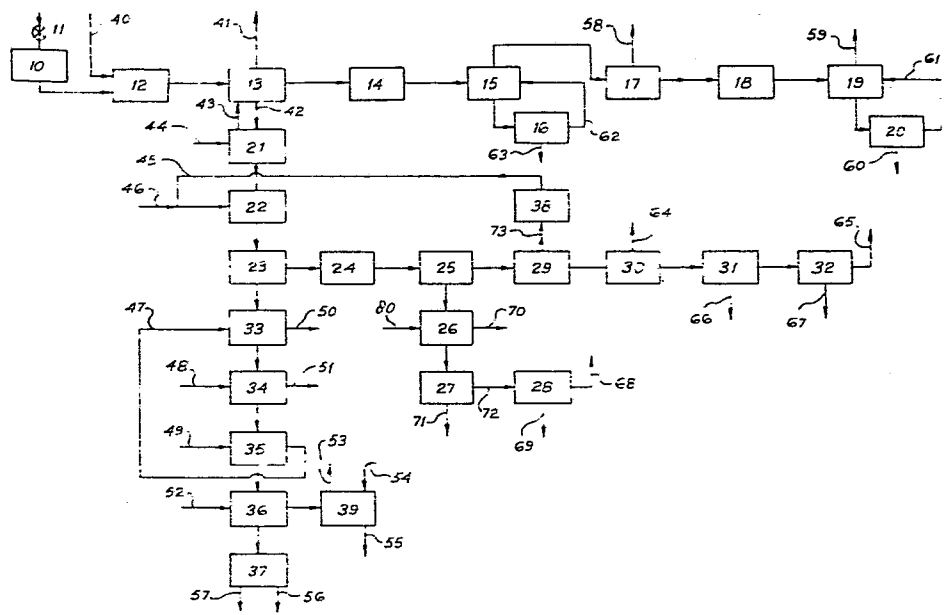
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⑤④ Coal de-ashing process.

⑤⑦ Valuable minerals or carbonaceous fuels are often not recoverable due to large quantities of presently inseparable undesirable substances. Silica, alumina, sulphur compounds and iron oxides often comprise the unwanted substances. There is thus provided a process for removal of these substances by the use of hydrogen fluoride wherein substantial amounts of the hydrogen fluoride may be recovered for recycle to make the process viable.

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"Coal De-Ashing Process"

This invention relates to a process for removing silica and/or aluminium bearing mineral matter and other reactive substances from substances which do not react with hydrogen fluoride under the same conditions. The reaction with hydrogen fluoride may be in the gaseous or liquid form.

It has been known that hydrogen fluoride particularly as a liquid will react with silica and dissolve same selectively from non-reactive materials such as carbonaceous matter, for example, coal. However, whilst this reaction has been known it has never been able to be put into a commercial viable process. The main reasons for this being that hydrogen fluoride is a particularly dangerous substance and any wastes produced which include hydrogen fluoride create troublesome disposal problems. Furthermore, hydrogen fluoride is a very expensive material and the known processes are ~~now~~^{not} economically viable because they have not shown how the hydrogen fluoride may be recovered and recycled.

Many carbonaceous materials, such as coal, oil, tar sands and oil bearing shales contain a valuable high energy component i.e., the carbonaceous material, incorporated with either chemically or physically bound substances which are not desirable because they are merely ash substances or create pollution problems. Such undesirable substances are substantially silicon, aluminium and sulphur compounds. These components make up the major unwanted matter in coal and other carbonaceous fuels.

Many coals contain ash contents up to 30% or even in excess of that figure. It is thus desirable that these coals have their ash contents reduced to amounts which are more acceptable to the fuel burning consumer. Low ash coals and other fuels, i.e. with ash contents below 1%, are very rare and very hard to obtain by conventional methods. However, these fuels are becoming more in demand due to the need to be able to burn them directly as a pulverised coal in situations such as diesel engines, built up areas and other critical fuel burning apparatus. The conventional methods of cleaning coal such as washing are generally not

satisfactory to reduce the ash content to the low levels required for the vast majority of coal that is available.

Furthermore, certain elements, such as gold, are non-reactive with regard to hydrogen fluoride. Thus, elements which are unreactive with HF under certain conditions also utilise the process of the invention for recovering from reactive associated components such as silicon, aluminium, sodium or other mineral matters.

It is thus an object of this invention to ameliorate the abovementioned disadvantages.

In one broad form the invention provides a process for separating compounds or elements which do not react with hydrogen fluoride from elements or compounds which do react with hydrogen fluoride, and recovery for reuse of substantial amounts of the hydrogen fluoride, said process comprising: (a) reacting feed material with hydrogen fluoride; (b) separating the resultant product into a gaseous stream and a solids or liquid stream, characterised in that (c) the gaseous stream is contacted with water at a temperature and pressure sufficient to reverse the original reaction to regenerate hydrogen fluoride gas and (d) separating the hydrogen fluoride gas from the solids and liquid thus formed; and (e) treating the solids-liquid stream from the initial reaction (a) by dissolving in aqueous hydrogen fluoride solution their compounds and/or elements that will dissolve in said solution and (f) separating out those that will not dissolve, (g) washing the undissolved solids to remove hydrogen fluoride solution and soluble fluorides from said solids and (h) recovering said solution of fluorides for reuse; (i) treating the liquid stream containing soluble fluorides from step (e) at a temperature and pressure to drive off the hydrogen fluoride as a gas to be recycled following condensation.

In a further broad form the invention provides a process for substantially removing silica and sulphur from coal comprising the steps of contacting coal with hydrogen fluoride gas for a time sufficient to convert substantially all of the silica, alumina and sulphur components to fluoride compounds, at a temperature from 32 to 300°F, separating

the gaseous components from the coal solids, collecting the coal solids; contacting the separated gaseous component with water at a temperature and pressure such that hydrogen fluoride is not soluble in water to precipitate sulphur and sulphur compounds from the gas, passing the remaining gas through a heater to raise the temperature of the gas to a sufficient temperature before contacting the gas for a second time with water to precipitate silica from the gas and convert the fluorine to gaseous hydrogen fluoride for recycle.

The invention will now be described by way of example only with reference to the accompanying drawing, which is a flow sheet diagram of the process of the invention with particular reference to coal in accordance with the preferred form of the invention.

The invention is to be described by its application to fine dried coal, however, it will be obvious that normal experimental procedure will establish the variables to be used with regard to feeding other materials to be processed instead of coal.

Dry fine coal, preferably less than 200 mesh and less than 1% moisture, is fed by means of a vacuum lock feeder into the coal feed bin 10 from where it is metered into a primary reactor 12. The primary reactor 12 may be a rotary ball mill to further grind the coal to finer particles whilst the reaction is being carried out. Also introduced into the primary reactor 12 is gaseous HF which is mixed with the coal at a temperature range from 32 to 300°F. The reactor 12 and obviously the other components in the system must be constructed of a material resistant to HF. Very few materials are suitable. Iron is suitable as long as the HF is concentrated, however it is attacked by dilute aqueous HF.

The reaction which takes place in the reactor 12 is allowed to continue for a sufficient time according to the nature of the feed component before being passed into a separator 13. The separator 13 produces initially two and in a more advanced form, three streams. The two main streams are a solid stream 42 and a gas stream 74.

The solid stream comprises coal, any unreacted ash, fluorides of aluminium, copper, magnesium, manganese, titanium, potassium, sodium and iron. Some low density gases such as included HF, and water and some of the higher density gases which are produced by the reaction such as fluorides of silicon and sulphur will obviously also be included with the solids stream 42, either absorbed onto the surface or in the pores of the reacted solids.

The nature of the reaction basically relies on the known reaction of HF with various reactive solids to produce the fluorides thereof. The gaseous stream from the separator 13 is preferably passed through a filter to remove entrained solids and is divided into two streams 41 and 74, one of lighter gases 41 and one of the heavier gases 74. The reaction in the reactor 12 produces gaseous fluorides of certain compounds or elements under particular conditions of temperature, from 32 to 300°F, and pressure suitable for the appropriate temperature. With coal the main fluorides formed in the gaseous state are silicon fluorides and sulphur fluorides. Some gaseous arsenic fluorides may also be formed.

It is preferable to form silicon tetrafluoride and sulphur tetrafluoride in the gaseous form. The gaseous stream from the reactor 13 as mentioned above is divided into a light stream 41 and a heavy stream 74, the light stream comprising substantially hydrogen fluoride gas which is the excess gas from the reaction and any water vapour in the gaseous form. The gaseous stream 74 of heavier gases i.e. the silicon and sulphur fluoride gases leaving the separator 13 is heated and compressed in a compressor 14 to a temperature of from 220°F to 260°F at a pressure from 60 to 100 psig and is then contacted following this compression with liquid water at similar temperature and pressure in a contacting vessel 15.

In the water-contacting vessel 15 the fluorides of sulphur react to form non-gaseous sulphur crystals or sulphur compounds. The reduction of the sulphur from its fluoride form forms hydrogen fluoride gas which is basically the reverse of the reaction from the formation of the sulphur

fluorides back in the reactor 12. Thus, a certain amount of the HF gas has been regenerated at this point. At this temperature and pressure the hydrogen fluoride solubility in water is low.

5 The liquor from the contacting vessel 15 is withdrawn from the bottom thereof and treated to remove 63 the sulphur-bearing compounds by way of say filtration 16 and the spent liquor is recycled 62 back to the vessel 15. The sulphur compounds are thus removed 63 from the system. The
10 gaseous stream then leaves the vessel 15 containing substantially silicon tetrafluoride, water and hydrogen fluoride gas, the water being in the gaseous form. Partial separation of these components is achieved in a density separator 17 with HF (g) and H₂O (g) being extracted. The remaining gaseous
15 stream from separator 17 containing silicon fluorides and gaseous water is heated to a temperature from 800°F to 900°F at a pressure from 60 to 100 psig in a vessel 18. Furthermore, in vessel 18 the gas is contacted with liquid water at a temperature from 220°F to 260°F and 60 to 100 psig in
20 vessel 19. The silicon tetrafluoride is reduced in this vessel 19 to silicone dioxide (silica) and the HF gas is thus regenerated. The liquor from contacting vessel 19 is withdrawn from the vessel, filtered 20 or passed through any other liquid separation means and the silicon crystals and
25 other solids are removed 60. The spent liquor 21 from the solid liquid separator 20 is returned to the vessel 19.

As the process proceeds the aqueous liquor which passes through vessels 15 and 19 becomes saturated with trace compounds which are being carried over in the gas
30 stream from the separator 13. These trace compounds are removed from the process by bleeding liquor (not shown) from the two loops. The solids stream 42 from the separator 13 is countercurrently purged 44-43 with gaseous HF in vessel 21. This prevents the carrying over of any other
35 gases in the stream as it passes for further processing of the solids material. The solids from vessel 21 are fed into a secondary reactor 22. In the secondary reactor 22 the solids are mixed with aqueous HF solution 46 which is preferably maintained at around 20 to 30 mass percent HF

concentration. In the reactor 22 the solid fluorides of aluminium are dissolved and any unreacted alumina from the primary reactor 12 is also dissolved. Virtually all other coal ash derived solids from the primary reactor 12 are also dissolved, the coal remains undissolved and untouched by the HF. The mixed liquid-solid stream from the secondary reactor 22 is thus drawn off and fed to a solid-liquids separator 23 such as a settling tank. In the separator 23 the solids are removed from the liquor. The liquor from the separator 23 is then passed through a heater 24 which raises the stream temperature and pressure to from 220 to 260°F and from 60 to 100 psig, thereby reducing the solubility of the HF gas and hence the solubility of fluorides of aluminium, calcium, magnesium and manganese causing these materials to crystallise. The remaining stream is then fed to a solids-liquid separator 25 where the solids are separated from the liquid-gas stream. The solid stream from the settler 25 is washed with water 80 in washer 26 to remove, in stream 70, traces of HF and water soluble fluorides. The solids are then heated in heater 27 to a temperature from 2200° to 2400°F at which temperature the fluorides of aluminium vaporise. These vapours are drawn off 72 from the heater 27 and condensed to form solid aluminium fluoride 69 in condensor 28. The residue in heater 27 is cooled to solids 71 which are predominantly oxides and/or fluorides of magnesium, manganese, calcium and aluminium. The liquor-gas stream from settler 25 contains dissolved fluorides of titanium, potassium and sodium. This stream is split in gas-liquid separator 29 with the bled liquid stream fed to evaporator 30, in which the dissolved solids are concentrated and then fed to heater 31 at 500 to 700°F. Steam generated in the evaporator 30 is passed to the atmosphere through line 64.

In heater 31 the fluorides of titanium vaporise. These vapours are drawn off from the heater 31 and condensed to solid titanium fluoride 67 in condensor 32.

The residue in heater 31 is removed 66 and cooled to solids, predominantly fluorides of potassium and sodium.

Solids from settler 23 are predominantly coal with

traces of iron which are wet with aqueous HF solution. The total non-gaseous stream from settler 23 is washed in water 47 in washer 33 followed by washing with diluted ammonia solution 48 in washer 34. The stream is then passed to
5 vessel 35 where it is again washed in water 49. The ammonia wash 34 dissolves residual hydrogen fluoride and fluorides from the coal. The wash water liquor is preferably conducted in a countercurrent manner with regard to vessels 33 and 35 thus it is recycled 47 from vessel 35 to vessel 33.

10 The washed coal is then dried by hot air 52 in dryer 36 and fed to separator 37 for removal of iron 56 by density separation.

The main stream 73 from the splitter 29 is cooled in heat exchanger 38 to redissolve the hydrogen fluoride
15 vapours in water. This regenerates aqueous HF solution for recycle 45 back in the secondary reactor 22.

Hydrogen fluoride and water gas mixtures from stages 13, 17, 19, 28 and 32 are thus recycled as feed to stages 12 and 21. Dilute hydrogen fluoride from stages 26
20 and 33 is concentrated by distillation for reuse in stage 22. Hydrogen fluoride vapour in the air stream from dryer 36 is removed by scrubbing with aqueous lime in tower 39.

The above preferred embodiment has described the process for utilising hydrogen fluoride for the extraction
25 of coal from its unwanted ash and other pollutant-type materials. Using the above method it is possible to obtain ash contents of less 0.1%. Of course the degree of ash remaining is determined on a number of factors, the main ones of which are the degree of reaction of the initial
30 reactor and the efficiency of the separation stages and the second reaction stage. Whilst it is preferred to use fine powdered coal, experiments conducted using lump coal material of the fine powdered coal have proven to be about equally as effective. The hydrogen fluoride effectively
35 reacts with the included ash in the cost to leave a honey-combed clean coal structure.

The above process can also be used to recover oil from tar sands and shale oil deposits. By feeding tar sands or ground shale containing shale oil into the primary



reactor 12. basically the same reactions occur as with coal. The "oil" may thus be extracted along the path of the coal solids with minor variations to the detailed parts of the process in an oil form. In all of the above processes the amount of HF which is required of fresh make up to the system after allowing for recycle, will also depend upon how the various fractions of the by-products are removed from the process for example it may be very desirable to remove magnesium and aluminium in a fluoride form. Particularly, aluminium fluoride which is a valuable by-product as it is an intermediate material in the alumina process, thus, its value in the aluminium fluoride form may well exceed its value in returning to an alumina form and recovering the fluorine for reconstitution to HF.

The process may furthermore be used for the extraction of metal values from ore deposits which comprise substantial amounts of silica and/or iron oxide and/or magnesium oxides. As there are many low grade mineral deposits which contain large amounts of valuable metals in low concentrations suitable economic recovery methods at present are not available.

The majority of mineral processing methods require the use of large quantities of water for treating the minerals. This obviously is a problem in dry areas of the world where water is in very short supply, thus low grade ores as they are too expensive to transport in their unconcentrated state cannot be processed at the mine site and are thus not presently of any real value. Furthermore, large water use requires large energy use which further reduces the viability of any recovery metals from low grade deposits.

Mined ore usually contains as major constituent silica which may in its various forms make up to 90% or more of the ore. If silica is not the major component then iron oxide is often a major component. Iron oxide is usually present with silica in most deposits. Therefore, to concentrate the valuable minerals contained in up to 10% of the ore it is essential to separate these minerals from silica and iron oxide.

The above prescribed process for treatment of coal is thus applicable to silica, magnesium, iron-type ores. The ore which has been mined aground to an acceptable size is fed into the process in the same manner as is the coal.

5 The hydrogen fluoride in the reactor 12 converts silica, sulphur and arsenic compounds to gaseous fluoride compounds. These gases are removed from the reactor after passing through separator 13. The gases may be treated in identical manner to the treatment of gases in the above described process for coal. The solid products from the separator 13 are removed and passed to a solids separation device 22 which may separate the solids of a specific gravity basis. Most of these solids are metal fluorides and include those metals which comprise nearly all of the valuable metals likely to be included in the ore, such as chromium, titanium, cobalt, silver, nickel, tin, lead, copper, gold and other rare metals. Some metals may require catalytic or temperature variations in the reactor to cause conversion to fluoride form. These variables are obviously a matter particular to the type of metal which is to be extracted or converted to fluoride. It is possible to selectively reclaim metal fluorides formed because they nearly all have significantly different solubilities. Thus separation by contact with water in some cases temperature and pressure variations will cause precipitation of certain metal fluorides and thus recovery of same following concentration by carrying out the reverse step of the reaction which formed the metal fluoride, the metals can be reclaimed in their concentrated form.

30 It is to be noted that iron oxides do not react with concentrated hydrogen fluoride in the acid form or gaseous form, however, they do react with dilute hydrogen fluoride in liquid form, therefore ^{if} ~~it~~ contact of the iron oxides is only with the gaseous hydrogen fluoride then no reaction takes place with the iron and these iron oxides may be cleaned free of all other elements that have reacted with the HF gas, which means that they can then be passed for use as a raw material for steel production or just simply removed from the valuable metal.

It is to be noted that in the above process there is substantial recycle of HF and valuable by-products are also produced, thus allowing the viability of the process to be proven.

Claims

1. A process for separating compounds or elements which do not react with hydrogen fluoride from elements or compounds which do react with hydrogen fluoride, and recovery for reuse of substantial amounts of the hydrogen fluoride, said process comprising: (a) reacting feed material with hydrogen fluoride; (b) separating the resultant product into a gaseous stream and a solids or liquid stream, characterized in that (c) the gaseous stream is contacted with water at a temperature and pressure sufficient to reverse the original reaction to regenerate hydrogen fluoride gas and (d) separating the hydrogen fluoride gas from the solids and liquid thus formed; and (e) treating the solids-liquid stream from the initial reaction (a) by dissolving in aqueous hydrogen fluoride solution their compounds and/or elements that will dissolve in said solution and (f) separating out those that will not dissolve, (g) washing the undissolved solids to remove hydrogen fluoride solution and soluble fluorides from said solids and (h) recovering said solution of fluorides for reuse; (i) treating the liquid stream containing soluble fluorides from step (e) at a temperature and pressure to drive off the hydrogen fluorides as a gas to be recycled following condensation.

2. The process of claim 1 characterized in that the gaseous stream prior to being fed to step (c) is separated to remove hydrogen fluoride gas for cycle.

3. A process for substantially removing silica and sulphur from coal comprising the steps of contacting coal with hydrogen fluoride gas for a time sufficient to convert substantially all of the silica, alumina and sulphur components to fluoride compounds, at a temperature from 32 to 300°F, separating the gaseous components from the coal solids, collecting the coal solids; contacting the separated gaseous component with water at a temperature and pressure such that hydrogen fluoride is not soluble in water to precipitate sulphur and sulphur compounds from the gas, passing the remaining gas through a heater to raise the

temperature of the gas to a sufficient temperature before contacting the gas for a second time with water to precipitate silica from the gas and convert the fluorine to gaseous hydrogen fluoride for recycle.

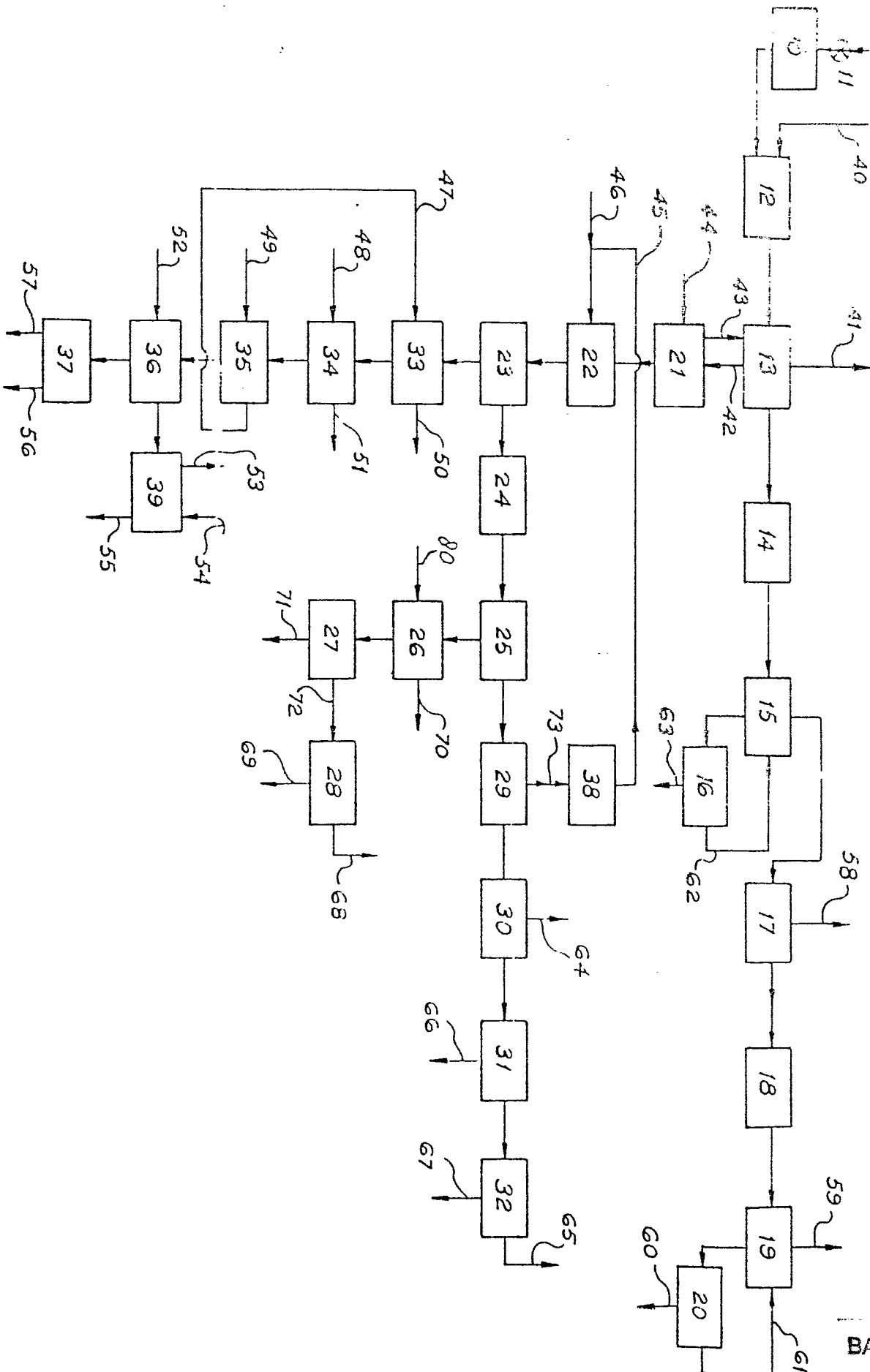
4. The process of claim 3 characterized in that the step of contacting the gaseous stream with water to precipitate out sulphur and its compounds is carried out at about 240°F and about 80 psig.

5. The process of claim 4 characterized in that the remaining steps of the process following the sulphur precipitation step are carried out at about 240°F and about 80 psig.

6. The process of claim 3 characterized in that the solids stream from said solids-gas separation step is washed in aqueous HF solution, to dissolve substances soluble in HF, passed through a solids-liquid separator, recovering the solids, washing the solids to remove dissolved compounds of hydrogen fluoride; recovering the coal solids and recovering the fluorides from the liquid streams for recycle.

7. The process of claim 6 characterized in that before final recovery of the coal, the coal is separated from the iron solids present.

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European Patent
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EUROPEAN SEARCH REPORT

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Application number

EP 80 30 0800

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | CLASSIFICATION OF THE APPLICATION (Int. Cl.) |
|--|--|----------------------------------|---|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | |
| A | <u>US - A - 2 624 698</u> (HICKEY) * Claims 1-8 * -- | 1 | C 10 L 9/02 C 22 B 1/00// C 22 B 11/00 |
| A | <u>GB - A - 115 630</u> (RIDONI et al.) * Claims 1-3 * -- | 1 | |
| A | <u>US - A - 1 380 458</u> (WOODRUFF et al.) * Claims 1-3; page 1, lines 19-33 * -- | 1 | |
| A | <u>FR - E - 95 128</u> (MAYOR et al.) * Abstract * -- | 1 | TECHNICAL FIELDS SEARCHED (Int. Cl. 7) C 10 L 9/02 C 22 B 1/00 1/02 3/00 11/02 11/04 C 01 B 31/02 |
| A | <u>US - A - 4 086 084</u> (OLIVER et al.) * Claim 11 * ---- | 1 | CATEGORY OF CITED DOCUMENTS X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons &: member of the same patent family. corresponding document |
| <input checked="" type="checkbox"/> The present search report has been drawn up for all claims | | | |
| Place of search | | Date of completion of the search | Examiner |
| The Hague | | 12-06-1980 | MEERTENS |