This invention is a novel apparatus which forms part of a hydrocarbon catalytic conversion system and provides the vessels and automatic controls for treating a regenerated catalyst by a series of procedures designed to remove metal contaminants.

Large quantities of mineral oil petroleum crudes, fractions thereof, and hydrocarbons derived therefrom, contain harmful amounts of metal impurities, such as nickel, vanadium and iron. These impurities are frequently present in such large amounts that utilization of the hydrocarbons is a real problem since the metals accumulate on catalysts in cracking, adversely affecting the product distribution of cracking yields by increasing coke and gas make and decreasing gasoline make. Thus catalytic cracking of the hydrocarbons is uneconomical because the metal impurities harmfully affect selectivity of the catalyst. For this reason, such stocks have not heretofore been utilized to the fullest possible extent, although the need has been expressed in the art for a feasible process for the catalytic cracking of petroleum residua or similar heavy hydrocarbon feeds. The chief deterrent to catalytic cracking of residua by conventional means has been the severe catalyst contamination, due to contaminant metals in many stocks, which leads to poor catalyst activity and often to poor product distribution and otherwise reduces the desired effectiveness of the catalyst. Although referred to as "metals," these catalyst contaminants may be in the form of free metals or relatively non-volatile metal compounds. It is to be understood that the term "metal" used herein refers to either form.

Various petroleum stocks have been known to contain at least traces of many metals. For example, Middle Eastern crudes contain relatively large amounts of metal components, while Venezuelan crudes are notable for their vanadium content and are relatively low in other contaminating metals such as nickel. In addition to metals naturally present, including some iron, petroleum stocks have a tendency to pick up tramp iron from transportation, storage and processing equipment. Because most of these metals, when present in a stock, would deposit in a relatively non-volatile form on the catalyst during the conversion processes and regeneration of the catalyst to remove coke would not remove these contaminants, such feeds are generally avoided. Iron, nickel, vanadium and copper, for example, markedly alter the selectivity and activity of cracking reactions if allowed to accumulate, producing a higher yield of coke and hydrogen at the expense of desired products, such as gasolines and butanes.

Catalytically promoted methods for the chemical conversion of hydrocarbons include cracking, hydrocracking, reforming, hydroforming, etc. Such reactions generally are performed at elevated temperatures, for example, about 300 to 1200°F, more often 600 to 1000°F. Feedstocks to these processes comprise normally liquid and solid hydrocarbons which at the temperatures of the conversion reaction are generally in the fluid, i.e., liquid or vapor, state and the products of the conversion frequently are lower-bolling materials. In particular, cracking of heavier hydrocarbon feedstocks to produce lighter hydrocarbon products requires that the gasoline range is widely practiced and uses a variety of solid oxide catalysts to give end products of fairly uniform composition. Cracking is ordinarily effected to produce gasoline as the most valuable product by conversion of about 40-80% of higher boiling materials to lower boiling fractions, and is generally conducted at temperatures of about 750 to 1100°F, preferably about 850 to 950°F, at a pressure up to about 2000 psi, preferably about atmospheric to 100 psi, and without substantial addition of free hydrogen to the system. In addition, feedstock is usually a mineral oil or petroleum hydrocarbon fraction such as straight run or recycle gas oils or other normally liquid hydrocarbons boiling above the gasoline range. These charge stocks, containing more than about 1.5 parts per million of vanadium and/or more than about 0.6 part per million of nickel are generally avoided in cracking processes and most refiners prefer less than about 0.5 part per million of vanadium or about 0.2 part per million of nickel in the cracking stock. Metal contents above these ranges may be present in feeds using the apparatus of this invention, it will be apparent that oils having metal contents in these generally undesirable ranges are the oils which this invention salvages. A mixture of vanadium and nickel may be considered as harmful as a single metal even though the individual amounts of such metals are below the values mentioned above because the effect of the metal components is frequently sufficient to give harmful effects during catalytic cracking. In most cases, however, the total of one, or both of these metals in the residual will be at least about 0.3 p.p.m. The maximum amount of metals in, for example, petroleum residua feedstocks can vary widely; most often the maximum amount of these poisoning metals in a residual stock will not exceed about 50 p.p.m. nickel and about 100 vanadium.

Solid oxide catalysts, both naturally occurring activated clays and synthetically prepared gel catalysts, as well as mixtures of the two types, have long been recognized as useful in catalytically promoting conversion of hydrocarbons. A popular "natural" catalyst is "Filtilt" which is acid-activated montmorillonite. For cracking processes, the solid oxide catalysts which have received the widest acceptance today are usually activated or calcined predominantly silica or silica-based e.g., silica-alumina, magnesia, silica-zirconia, etc., compositions, in a state of slight hydration and containing small amounts of acidic oxide promoters in many instances. The oxide catalyst may be alumina- or silica-based and ordinarily contains a substantial amount of a gel or gelatinous precipitate comprising a major portion of silica and at least one other material, such as alumina, zirconia, etc. The use of wholly or partially synthetic gel catalysts, which are more uniform and less damaged by high temperatures in treatment and regeneration, is often preferable. Popular synthetic gel cracking catalysts generally contain about 10 to 30% alumina. Two such catalysts are "Acrocat" which contains about 13% Al₂O₃ and "High Alumina Nalear" which contains about 25% Al₂O₃, with substantially the balance being silica. The catalyst may be only partially of synthetic material; for example it may be made by the precipitation of silica-alumina on clay, such as kaolinite or halloysite. One such semi-synthetic catalyst contains about equal amounts of silica-alumina gel and clay.

The apparatus of this invention is contemplated for use with fluidized beds of catalyst. Such catalysts are generally in the form of a powder, frequently in a size range of about 20 to 150 microns. It is often difficult to work with and has an abrasing action on equipment. In the case of gas pumps which are required to have close tolerances, such abrasive action leads to early failure, and the catalyst also is damaged to some extent. In conventional fluidized beds gases are used to keep the catalyst in the form of a dense turbulent bed which has no definite upper interface between the dense
3. (solid) phase and the suspended (gaseous) phase mixture of catalyst and gas. In this invention apparatus is provided wherein catalyst flow is performed by air induced by gravity and only when it is in the form of a slurry in a liquid are pumps used in its conveyance. The apparatus which this invention provides for removing metal contaminants from a catalyst comprises a catalyst regenerator, a treating chamber for contacting the catalyst with an oxygen-containing gas, a sulfiding catalyst chamber for contacting the catalyst with a sulfiding gas, a chlorinating chamber for contacting the catalyst with a chlorinating gas and a quench chamber for contacting the catalyst with an aqueous liquid. The invention also provides a novel apparatus for cooling the sulfided catalyst. Flow lines are provided for the catalyst between the chambers and the catalyst flow line between the chlorinating chamber and the quench chamber has a valve controlled by conditions in the quench chamber. The apparatus provides for catalyst flow through the vapor contact chambers to the quench chamber by gravity.

In a preferred modification of the apparatus of the invention the oxygen treating chamber, sulfiding chamber and chlorinating chamber each have means for determining the level of a bed of catalyst in the respective chamber and the flow lines have catalyst flow control means responsive to the bed level in each of the flow lines. This provides for the total flow of catalyst through the system to be controlled by the valve in the line between the chlorinator and the quench tank. The invention may also be provided with a cooling chamber for the catalyst between high temperature and moderate temperature vapor contact phases.

During most hydrocarbon conversion operations coke deposits on the catalyst. This coke is removed, generally, by subjecting the catalyst to treatment with air at an elevated temperature to burn the coke off. Regeneration of a catalyst to remove carbon is a relatively quick procedure in most commercial catalytic conversion operations. For example, in a typical fluidized cracking unit, a portion of catalyst is continually being removed from the reactor and sent to the regenerator for contact with air at about 950 to 1200° F., more usually about 1000 to 1150° F. Combustion of coke from the catalyst is rapid, and for reasons of economy only enough air is used to supply the needed oxygen. Average residence time for a portion of catalyst in the regenerator may be on the order of about two to six minutes and the oxygen content of the effluent gases from the regenerator is normally less than about 1/2%. Catalyst is generally removed from the conversion system—that is, the stream of catalyst which is cycled between conversion and regenerating operations—before the poison content exceeds about 500 to 10,000 p.p.m., the poisoning metals being calculated as their common oxides. Generally, at least about 250 or 500 p.p.m. vanadium and/or at least about 100 or 200 p.p.m. nickel will be accumulated on the catalyst before deactivation is warranted. A suitable amount, generally a small portion of the catalyst, is removed from the system and demetalized, preferably after the oxidation regeneration which serves to remove carbonaceous deposits. With a continuously circulating catalyst stream, such as in the ordinary “fluid” system, a slip-stream of catalyst may conveniently be removed intermittently or continuously from the regenerator standpipe. The severity of regeneration is generally such that the catalytically active catalyst contains not more than about 0.5% carbon.

A number of procedures have become available which provide for the removal of the common metal poisons nickel and vanadium from a contaminated hydrocarbon conversion catalyst. Such procedures frequently involve contact of the catalyst at elevated temperatures with vapors reactive with the poisoning metals and are described, for example, in copending applications Serial Nos. 758,681, filed September 3, 1958, now abandoned; 765,794, filed October 17, 1958; 849,199, filed October 28, 1958; 21,930, filed April 1, 1960; 39,810, filed June 30, 1960; 47,958, filed August 4, 1960; 53,380, filed September 1, 1960; 53,623, filed September 2, 1960; 54,368; 54,405 and 54,532, filed September 7, 1960, now abandoned; 55,129; 55,160 and 55,184, filed September 12, 1960; 1,753,073, filed December 2, 1960; 53,380, filed September 14, 1960; 67,518, filed November 7, 1960; and 73,197, filed December 3, 1960; all of which are herein incorporated by reference. It has been found, for example, that Ni, Fe and V may be removed from a catalyst by converting the materials into volatile compounds; a chlorination treatment can convert iron and vanadium to volatile chlorides, as reported in copending applications Serial Nos. 849,199 and 54,532, and nickel may be converted to the volatile nickel carbonyl by hydrogenation and treatment with carbon monoxide, as pointed out in co-pending application Serial No. 47,590.

It has also been found that Ni, Fe and V may be removed from a catalyst by certain aqueous media; a basic aqueous wash containing ammonium ions is suitable for removal of V poisons as reported in copending application Serial No. 39,810. The removal of nickel may be accomplished by washing the chamber to which fresh wash water is fed when the nickel is first converted into a compound dispersible in such a wash. The chlorination treatment can convert nickel to the soluble chloride form. Sulfidation of nickel-poisoned catalyst appears to have important effects in making more nickel available for removal, so that sulfidation, as described in copending application Serial No. 53,380 is employed before chlorination. Also, as pointed out in copending applications Serial Nos. 19,313 and 55,160, a preliminary treatment of the catalyst with molecular oxygen-containing gas is of value in improving the vanadium removed by subsequent procedures. The treatment may remove a substantial part of one or more of nickel, vanadium and iron. The withdrawal of catalyst from the cracking system can be on a continuous or intermittent basis and ordinarily the catalyst will not be allowed to accumulate more than about 5000 or 10,000 P.p.m. of poisoning metal from the catalytic system. Treatment of the regenerated catalyst with molecular oxygen-containing gas is preferably at a temperature at least about 50° F. higher than the regeneration temperature that is, the average temperature at which the major portion of carbon is removed from the catalyst. The temperature of treatment with molecular oxygen-containing gas will generally be in the range of about 1000 to 1800° F. but below a temperature where the catalyst undergoes any substantial deleterious change in its physical or chemical characteristics. The catalyst, as pointed out, is in a substantially carbon-free condition during this high-temperature treatment. If any significant amount of carbon is present in the catalyst at the start of this high-temperature treatment, the essential oxygen contact is that continued after carbon removal. The apparatus of this invention provides for holding catalyst in an oxygen treating chamber for an average residence time long enough to stabilize a substantial amount of vanadium in its highest valence state, as evidenced by a significant increase, say at least about 10%, preferably at least about 100%, in the vanadium removal in subsequent stages of the process. This increase is over and above that which would have been obtained if the other catalytic treatment steps without the oxygen treatment. The high temperature of the treatment is imparted to the oxygen-containing gas by passing it through a burner, where part of the oxygen content is used to burn fuel. The treatment gas contains oxygen as the essential active ingredient. The gas may be oxygen, or a mixture of oxygen with inert gases, such as air or oxygen-enriched air. The temperature of the gas entering the treating chamber is controlled by regulating the amount of fuel sent to the burner in response to the tem-
perature in the treating chamber. The partial pressure of oxygen in the treating gas may range widely, for example, from about 0.1 to 30 atmospheres, but usually the total gas pressure will not exceed about 25 atmospheres. The factors of time, partial pressure and extent of vanadium conversion may be chosen with a view to the most economical conversion. The oxygen partial pressure is regulated by controlling the supply of the gas, for example, air, to the treating chamber.

In this invention part of the treating gas is used for conveying the regenerated catalyst to the treating chamber. The length of the time of treatment is controlled by determining the optimum bed level of catalyst in the treating chamber. Once this level is established the feed of regenerated catalyst is regulated to maintain the level. It is preferred to continue the oxygen treatment for at least about 15 or 30 minutes with a gas containing at least about 1%, preferably at least about 10% oxygen.

A sulfiding can be performed by contacting the poisoned catalyst with elemental sulfur vapors, or more conveniently by contacting the poisoned catalyst with a volatile sulfide, such as H₂S, CS₂ or a mercaptan. The contact with the sulfur-containing vapor is performed at an elevated temperature generally in the range of about 500 to 1500°F, preferably about 800 to 1300°F. The sulfiding conditions can include a sulfur-containing vapor partial pressure of about 0.1 to 30 atmospheres or more, preferably about 0.5 to 2 atmospheres. Hydrogen sulfide is the preferred sulfiding agent. The temperature of sulfiding may be achieved simply by preventing heat loss in the catalyst after the treatment with molecular oxygen-containing gas. Heat is also conserved for the sulfiding by warming some or all of the sulfiding gas before its entrance to the sulfider. This is conveniently done by passing lime or all of the sulfiding gas in counter-current contact with the hot catalyst in a countercurrent fluidized system. The gas serves to cool the catalyst preparatory to chlorination, which takes place at a temperature lower than sulfidation, as well as to warm the sulfiding gas. Proportioning of the sulfiding gas to the cooler and directly to the sulfider is established by flow responsive controls to give the proper temperature in the sulfider.

Flow of catalyst to the sulfider is by gravity and is controlled in accordance with the hold-up time desired in the sulfiding procedure. The time of contact may vary on the basis of the temperature and pressure chosen and other factors such as the amount of metal to be removed. The sulfiding may run for, say, up to about 20 hours or more, depending on these conditions and the severity of the poisoning. The proper bed level to give the hold-up desired is established in the sulfider and a differential pressure controller, operated by the differences in pressure at different levels of the bed, is employed to control the valve which permits flow of oxygen-treated catalyst to the sulfider. Temperatures of about 900 to 1200°F and pressures approximating 1 atmosphere or less seem near optimum for sulfiding and this treatment often continues for at least 1 or 2 hours but the time can depend upon the rate of gas diffusion within the catalyst matrix. Effluent vapors from the sulfider are generally incinerated. The sulfiding step performs the function not only of supplying a sulfur-containing metal compound which may be easily converted to the chloride form but also apparently serves to concentrate some of the other gases, especially nickel, at the surface of the catalyst particle. In addition, some of the poisoning metal-sulfur compounds may be removed from the catalyst during sulfiding, especially when the catalyst contains both nickel and vanadium.

Sulfided catalyst flows to and through the cooler by gravity. The principal cooling effect on the catalyst is due to indirect heat exchange of the catalyst with a coolant fluid. However, in the novel cooling device employed in this invention heat transfer from the catalyst to cooler gases is improved by maintaining the catalyst in a fluidized condition while passing through the cooler. Under fluidized conditions remarkably high rates of both mass and heat transfer prevail. The novel cooler exploits these effects by providing for entry of the hot catalyst at the top of a finned-tube heat exchanger and passage of the catalyst downwardly within the tubes countercurrent to both the main cooling fluid passing upwardly on the outside of the tubes and a gas passing upwardly through the inside of the tubes at a fluidizing velocity. The main cooling fluid is air, while the fluidizing gas is a sidestream of the sulfiding vapor. The extent of catalyst cooling is determined by the rate of cooling fluid flow and this rate may conveniently be controlled automatically by the temperature prevailing in the chlorine stream.

Treatment of the cooled, sulfided, metals-contaminated catalyst with a chlorinating agent at a moderately elevated temperature is of value in removing vanadium and iron contaminants from the catalyst as volatile chlorides and converting nickel to a water-soluble form. This treatment is described in copending application Ser. No. 849,199. Generally, the major proportion of the volatile chlorides is removed during contact with the chlorinating vapor. The conversion to chlorides makes use of vapor phase chlorination at a moderately elevated temperature at wherein the catalyst composition and structure is not materially altered by the treatment. A substantial amount of the poisoning metals content is converted to chlorides. The chlorination takes place at a temperature of at least about 300°F, to say about 1000°F, preferably about 530 to 650°F, with optimum results being obtained close to about 600°F. The chlorinating reagent is a vapor which contains chlorine, preferably in combination with a carbon or sulfur compound promoter. Such reagents preferably are the chlorine-substituted light hydrocarbons, such as carbon tetrachloride, which may be used as such or formed in situ by the use of, for example, a gaseous mixture of chlorine gas with low molecular weight hydrocarbons such as methane, ethane and propane. The chlorinating agent is essentially anhydrous, that is, if put in the liquid form no separate aqueous phase would be observed. The chlorination may take about 5 to 120 minutes, more usually about 20 to 60 minutes, but shorter or longer reaction periods may be possible or needed, depending on the linear velocity of the chlorinating and purging vapors. Such time control is established by determining the optimum depth for the bed for catalyst in the chlorinating reactor. This bed level is controlled, as are the other beds mentioned, by the use of a differential pressure controller governed by pressures in different levels of the bed of catalyst in the chlorinator which in turn controls the entry of catalyst to the chlorinator by governing operation of a valve in the line between the cooler and the chlorinator.

The apparatus includes a chlorinating vapor feed system which includes a mixing conduit connected to a source of chlorine or hydrogen chloride, the flow of which to the mixing conduit is automatically controlled. Also leading to the mixing conduit are a vaporizer and pump which are connected to a source of promoter, e.g., carbon tetrachloride.

The apparatus includes means for disposing of excess effluent vapors from the chlorinator. In the disposal apparatus effluent chlorination vapor containing various metal, chlorine and sulfur compounds is withdrawn from the chlorinator by a line leading to a gas-liquid contact chamber. In this scrubber the chlorinated catalyst is passed countercurrently to water which lowers the vapor temperature, condenses any volatile materials such as sulfur or vanadium and iron chlorides, which are sent to waste. Flow of water to the scrubber may be automatically controlled to give a reasonable temperature to water leaving the bed of catalyst. Effluent vapor from the scrubber, containing HCl, Cl₂ etc., is passed to a neutralizer. This vessel, which may be provided with beds of inert solid contact material,
may be supplied at the top with a neutralizing reagent such as a strong caustic soda solution. The supply of water to the cooler and sulfider may be automatically controlled to permit minimum caustic usage. Waste from the neutralizer, which is basic, is combined with the acidic waste from the scrubber when passing to the sewer. It may be desired to have an excess of about 0.1 weight percent caustic in the combined liquid waste. This system is designed to neutralize the waste chlorine and flush out the metallic chlorides resulting from the chlorination. The separate scrubber is provided to avoid the deposition in the packing of the neutralizer of gelatinous metallic hydroxides.

After chlorination the catalyst is sent to a quench or slurry tank where it is contacted with an aqueous medium to remove from the catalyst nickel chloride produced in the chlorination procedure. This aqueous wash medium tends to be somewhat acidic, due to the presence of acid-acting chloride on the catalyst. In order to avoid undue solution of alumina from the catalyst, due to acid attack, contact time is preferably limited to about 3 to 5 minutes which is sufficient for nickel removal. Also, to avoid substantial alumina loss the pH of the material in the quench tank is controlled by the addition of ammonia water. The ammonia addition is automatically controlled in response to the pH of the catalyst slurry leaving the quench tank. Such control may be achieved by providing a slightly porous section of pipe in the line leading from the slurry tank. Some slurry liquid drips from this porous section into a surrounding conduit which constantly conducts samples to an electrode for pH measurement and control of the ammonia water supply to the slurry tank in response to the pH measurement.

Conditions in the quench or slurry tank are used as the primary determinant of catalyst flow in the entire demetallization system. Such conditions may be the temperature of the slurry, or the density of the slurry.

Temperatures from ambient temperature to the boiling point of water are generally sufficient for the chloride removal in this step of the demetallization procedure. The addition of catalyst having the moderately elevated temperature of the chlorination process increases the temperature of the slurry somewhat and this change may be sensed by a suitable device with which the apparatus of this invention may be supplied. Water is fed to the quench tank at a constant rate and a constant temperature. A heat exchange means is provided to give an even temperature by indirect contact of the water with steam. The variation of the slurry temperature in the quench tank from the temperature of the entering water, although due, to a slight extent, to the heat of acid neutralization by ammonia, is primarily due to the heat given off by the chlorinated catalyst. This, in turn, depends upon the rate of catalyst entry to the quench tank. The line for catalyst flow between the chlorinator and the quench tank is controlled by a valve responsive to the temperature in the quench tank. The temperature increment due to NH₃ neutralization is substantially additive in the whole range of catalyst flow rates with which the apparatus of the invention is designed to be used; therefore, the temperature control may be set up with an allowance for this heating phenomenon. The entry of catalyst to the quench tank, therefore, may be used to determine the hold-up time for catalyst in the bed in the chlorinator.

Alternatively the apparatus of this invention may be provided with an instrument such as a differential pressure recorder sensitive to the density of the slurry of the quench tank. Such a density response, coupled with a measurement of the slurry flow rate from the quench vessel, serves to activate the valve of the catalyst line from the chlorinator. Thus by either means, entry of catalyst to the quench tank determines the hold-up time of catalyst in the bed in the chlorinator, the bed level in the chlorinator controlling entry to the chlorinator from the cooler and sulfider, the bed level in the sulfider controlling entry from the oxygen treater, the bed level in the oxygen treater controlling withdrawal of poisoned catalyst from the regenerator standpipe, as described above. Vapors produced in the quench tank are conveniently sent to the scrubber and other parts of the chlorinator effluent vapor disposal system.

The slurry of catalyst in quench medium is pumped to a filter system. Exit of the slurry is permitted by a valve responsive to the liquid level in the quench tank. Where continuous filtration is desired, a pan filter may be used. In such a filtering means catalyst slurry travels along a screen where the liquid of the quench medium drains from it to a filtrate receiver. As it travels, wash water may be sprayed on the catalyst, the supply of wash water being automatically regulated. Alternatively, a two-stage drum filter may be employed for the filtration and washing of the filter cake. Vapors entrained in the filtrate in the receiver are removed by a vacuum pump responsive to pressure within the filtrate receiver. Filtrate may be discharged directly to a sewer or the slightly acid filtrate may first be neutralized with effluent from the neutralizer tower before disposal. Catalyst exists the filter to a slurry tank.

Batch filtration may be performed by providing two tanks having filter material across the bottom which are alternately supplied with catalyst slurry from the quench tank. A cycle timer is used to actuate valves in the proper sequence. While one tank is being filled with catalyst slurry from the quench vessel, the other is being used to wash a batch of catalyst. Pressure is applied to each tank by means of compressed air to provide a driving force for filtration. Wash water enters below the filter material several times each cycle and serves as a filter back-wash as well as a catalyst wash. Each wash is preferably prolonged for about 3 to 5 minutes for adequate diffusion time, that is, time to allow nickel chloride in the pores of the catalyst to diffuse into the water. A level switch is provided on each vessel to interrupt the supply of wash water when the proper level is reached in the vessel.

In either filtering operation, the filtered catalyst is passed to a slurry tank where it may be mixed with further water, again automatically controlled by the liquid level in the slurry tank, to provide a thin enough slurry to be pumped back to the regenerator. The operation of this pump is controlled to give a steady return of slurry to the regenerator.

The invention will be better understood by reference to the accompanying drawing in which FIGURE 1 represents a schematic of a hydrocarbon conversion catalyst regenerator with a demetallization system;

FIGURE 2 represents an alternate filtering system; and FIGURE 3 is a detailed vertical cross-section of the cooler.

In FIGURE 1 the main catalyst treating chambers employed in the system are the regenerator B, the oxygen treating chamber D, the sulfiding chamber F, the cooler H, the chlorinating chamber J, the quench vessel M, the filter P and the slurry tank R. In FIGURE 2 slurry tank R is shown with filters T and V.

The catalyst flow lines include regenerator standpipe 5 and regenerated catalyst line 10 which has the control valve 13. Oxygen-treated catalyst line 20 has the control valve 25. Sulfided catalyst line 20 and line 30 having the valve control 35 leads from chamber H to chlorinator I. Chlorinated catalyst line 37 contains the main flow control valve 40. Quenched catalyst slurry line 45 has the pump 44, which is provided with motor 45 and the control valve 46. In the embodiment of FIGURE 2, line 48 enters line 48 having the valve control 52 having the valve 55. Line 57, or in the embodiment of FIGURE 2, lines 62 and 64 having the valves 66 and 69 respectively, and line 70 conduct the catalyst filter cake to the slurry.
tank R. Catalyst slurry is conveyed back to the regenerator B by line 75 which contains the pump 77 which is operated by motor 78, and the valve 81.

Motive power for conveying the catalyst through the demetallization system is supplied by air in line 90 which is provided with the valve 95, while cooling effects on the air are provided by air in line 97, which has the valve 99, and leads to the condenser H.

The treating fluid system includes the oxygen-containing gas line 101, the exhaust gas line 102, sulfidizing gas by-pass line 105 which has the valve 109, the sulfidizing gas exhaust line 111 and incinerator 112 which has the air supply line 113, the sulfidizing gas supply line 114 and the fluidizing sulfiding gas line 115 which contains the valve 119.

Chlorinating vapor is conveyed to the chlorinating chamber J by the line 121 which blends chlorine, etc. flowing in the line 123 which is provided with the valve 128 and chlorinator promoter from line 130 which is provided with pump 133 which has the motor 134 and heater or vaporizer 135. Exhaust chlorinating vapor is removed from the chlorinator by line 137.

Quench tank M is supplied with water by the line 141 which has the heater 143 and valve 145. The quench tank M is also provided with line 150 to a pH adjusting fluid and this line is provided with valve 155. Line 157 is provided to convey exhaust gas from the quench tank.

The filter is supplied with wash water by the line 160 which has the valve 165. Filtrate is removed by line 168. Water is supplied to slurry tank R by line 174 which has the valve 175.

This invention also supplies means for treating the treating fluids which comprise the oxygen gas heater or burner 180, to which fuel is supplied by line 183, which has valve 185. Chlorinator effluent line 187 and quench tank vapor effluent line 197 lead to the scrubbing tower 191 which has baffles 192. Line 193 which has valve 199 conveys water to the scrubber. Line 202 is provided for removal of effluent vapors from the scrubber. This line leads to neutralization tower 204 which has granular packing material 206 and is supplied with caustic solution by line 208 which has the valve 212. Effluent vapor from the neutralizer leaves by line 214 to the atmosphere. Scrubbing tower 191 and neutralizing tower 204 are provided with lines 216 and 218 respectively, for removal of exhausted scrubbing liquid and neutralizing liquid to the catch basin 220 for the sewer. Line 168 leads to the filter receiver 222 which holds the filtrate for removal of entrained gases by the line 225 and vacuum pump 227 which has the motor 230, before releasing filtrate by line 232 to the catch basin 234 for the sewer.

In the demetallization system the motors 45, 78, 134 and 230 may be electric motors or steam turbines. The valves included in the device of the invention are in general automatically controlled, that is, controlled in response to conditions in the system. The control systems generally include a sensing mechanism and an impulse transmission line which can be electrical, pneumatic or hydraulic. Generally, pneumatic transmission systems are preferred. Also, similar systems are used to provide information, by way of indicators, to the operator of the demetallization unit.

The control and information systems include differential pressure indicating system 250, which senses at points 252 and 255 of the line 10; differential pressure control system 262 which controls actuation of valve 13 and senses at points 264 and 266 of the oxygen-catalyst differential pressure control system 278 which controls actuation of valve 25 and senses at points 280 and 282 of the sulfidizer F; differential pressure control system 292 which controls actuation of valve 35 and senses at points 294 and 296 in the chlorinator J. Pressure responsive control system 301 actuates steam valve or elevated 303 and senses at point 394 of the filtrate tank 222. The valve or switch 303 governs operation of the motor 230. Pressure responsive control system 305 controls operation of the valve or switch 307 and the motor 78 and senses at 308 in the demetallized catalyst slurry line 75. Likewise, pressure responsive control system 309 controls operation of the valve or switch 311 and motor 45 and senses at 312 in the slurry line 42.

Flow responsive control system 313 actuates the valve 95 in air line 90 in response to the flow rate in this line; temperature responsive control system 315 actuates the valve 185 in fuel line 183 in response to the temperature sensed at point 316 in oxygen treater D; flow responsive control system 317 controls valve 109 in response to the flow of sulfiding gas in line 105; flow responsive system 319 actuates the valve 119 in response to the flow of sulfiding gas in line 115; temperature responsive system 321 actuates the valve 99 in cooling air line 97 in response to the temperature sensed at point 322 in chlorinator J.

The principal control system of the invention is system 323 which actuates valve 40 in line 37 in response to temperature or density conditions in quench tank M. Temperature response may be achieved by employing system 323 with system 324 which senses the temperature at point 325 in quench tank M. Alternatively, system 323 may respond to switch 326 which senses pressure at point 327 in line 42 and senses the density of slurry in quench tank M obtained by differential pressure control system 328. Temperature pressure control system 328 also is able to actuate valve 46 in line 42 in response to the liquid level of quench tank M.

Flow responsive system 329 actuates valve 148 in response to flow in line 141; valve 330 in steam line 333 is actuated by temperature responsive system 334 which senses at 335 in line 141. Alternatively the valve 330 may be placed in a water by-pass line, not shown, to regulate the temperature of deaerating water flowing to the quench vessel.

pH responsive control system 337 actuates the valve 155 to govern the flow of pH adjusting material such as ammonia in line 159. This system includes the receiver electrode vessel 338 which is supplied with samples by line 339 which taps catalyst slurry line 42 perhaps by means of a porous pipe section as described above. Line 343 permits sample return to the quench vessel.

Flow responsive control system 347 actuates valve 199 in response to flow in line 193; flow responsive system 347 actuates valve 212 in response to flow in line 210; flow responsive system 349 actuates valve 128 in response to chlorine flow in line 123; flow responsive system 351 actuates valve 165 in response to flow in water line 169; control system 355 actuates valve 355 in line 171 in response to liquid level sensed at points 355 and 356 in slurry tank R. Motor 134 may also be controlled by the flow in promoter line 130 by suitable means, not shown. Motors are also supplied: 366, for stirrer 368 in quench tank M, 370 for stirrer 373 in slurry tank R, 375 for stirrer 377 in filter V and 350 for stirrer 383 in filter T.

The filter system shown in FIGURE 2 provides for batch filtration and washing of the catalyst from the quench vessel. A cycle timer is used to actuate the valves in the proper sequence. While one tank is being filled with catalyst from the quench vessel, the other is being used to wash a batch of the catalyst. Pressure or vacuum is applied to each tank, for example, by means of compressed air, to provide a driving force for filtration. Filters V and T are provided with lines 400 and 492 for back-washing several times per cycle with water from line 404. These lines have the valves 406 and 498, respectively. Filter V is provided with level switch 416 and filter T is provided with level switch 420 to cause the wash water valve to close when the proper level is reached.

In a typical operating sequence, catalyst slurry is transferred to vessel V through lines 330 and vessel T is being drained through valve 421. Outlet valve 421 is closed and water is introduced through valve 408. The slurry is agitated for several minutes then the vessel is drained.
through valve 421. Once more outlet valve 421 is closed and water is introduced through valve 408. After agita-
tion, valve 69 is opened and catalyst slurry proceeds through the line 70 to the slurry tank R. By this time vessel V is filled and the draining and restirring cycle is initiated. Line 70 may bypass slurry tank R and lead directly to the line 75.

Figure 3 shows the cooler H in greater detail. The cooler, as mentioned above, is supplied at its bottom with conduit 97 for the entry of cooling fluid, conduit 115 for the entry of fluidizing gas and conduit 30 for the exit of cooled solids. At its top the elongated vessel is supplied with the entry 27 for hot solids and with the exit 424 for cooling fluid. Also, the cooler may be supplied at the top with a separate exit 426 for fluidizing gas, although in this invention the fluidizing gas which performs the catalyst fluidization in the tubes passes from the cooler to the sulfider by way of solids entry line 27.

The cooling vessel is elongated, as mentioned, is constructed of materials chemically resistant to the materials handled, and preferably is provided with conical top and bottom sections 428 and 430 attached to a generally cylindrical shell 432. The vessel is provided with a plurality of tubes 434, having a small enough inside diameter to cause the fluidizing gas entering the bottom of the vessel to have fluidizing velocity. The upper coni-
cal section 428, may be separated from the interior of the vessel by any suitable means such as the header 436, which the tubes, 434, pierce. The tubes are joined at their bottoms to form the manifold section 440, which is connected to the solids exit conduit 30 and the fluidizing gas inlet conduit 115. The manifolding section may also have the conical bottom 442 and the porous plate 444 extending across the section. This porous plate serves the function, as do the other porous plates located in lines 139, F and G, of distributing the fluidizing gas across the bottom of the fluidizing vessel. The outsides of the tubes 434 are provided with the fins 448 to offer an extended surface for contact with the cooling fluid. As can readily be seen, hot solids flow downwardly inside the tubes countercurrent to fluidizing gas inside the tubes and cooling fluid flowing upwardly on the outside of the tubes.

The operation of the apparatus of the invention can be described under a specific set of operating conditions. The catalyst head of the oxygen treating vessel, which is about the same pressure as the top of the regenerator, overcomes pressure drop through the system and the pressure difference between demetallization vessels. For exam-
ple a pressure in the regenerator standpipe 5 of about 30 p.s.i.g. produces a pressure of about 22 p.s.i.g. at the top of a catalyst bed in a typical regenerator. 1640 standard cubic feet of air per hour from line 90 can lift about 836 pounds of catalyst per hour through line 10 to oxygen treat D. With about 16,300 standard cubic feet of air per hour passing through line 101 to a burner which liberates about 540,000 B.t.u.'s per hour a pressure of about 23 p.s.i.g. and a temperature of about 1300° F. may be maintained in the vessel D. 23,200 s.c.f. of ex-
haut gas per hour passes through line 102 to the regenera-
tor to maintain the pressure equilibrium. Ex-
emplary conditions in the sulfider are 1175° F. and 2
p.s.i.g. The catalyst in the cooler is, so far as pressure and fluidizing conditions are concerned, in effect the bot-
tom of the bed of catalyst in the vessel and most of the chamber 428. A fluidizing gas velocity in the cooler of only about 0.005 foot per second is needed to fluidize and can be, for example, about 0.1 foot per second. About 200 s.c.f. of H₂S gas may be sent to the sulfider per hour, and 20 s.c.f. to the cooler. A catalyst cooler having a capacity of about 115,000 B.t.u.'s per hour lowers the temperature of the 836 pounds of catalyst per hour from the sulfuring temperature of 1175° F. to the chlorinator entry temperature of about 630° F., by passing about 30,600 s.c.f./hr. of air at 100° F. in

indirect heat exchange contact with the catalyst in the cooler.

Catalyst head in the chlorinator J may in general be sufficient to raise the 2 p.s.i.g. pressure at the top of the bed to about 5.5 p.s.i.g. at the bottom of the chlorinator. When about 3.1 grams per hour of CCl₄ from line 130 are heated to 200° F. and mixed with C₂Cl₂ gas from line 133, 215 s.c.f./hr. of a promoted chlori-

nating agent are produced, having a temperature of about 170° F. The temperature of the quench tank M under average catalyst flow may be maintained at about 120° F. by supplying 9.52 barrel per hour of 85° F. water. About 2 p.s.i.g. is maintained in the quench vessel. About 4.6 lbs/hr. of NH₃ on a dry basis may be supplied to the quench tank to maintain a proper pH level.

Under such typical conditions 10.56 barrels of catalyst slurry may be sent each hour from the quench tank M to the filter P or the filters T and V. The use of 22.9

barrels of water per hour for washing the filter cake produces 30.5 barrels of filtrate per hour. The addition

of 3.6 barrels per hour of water in slurry tank R pro-

vides 6.58 barrels per hour of demetallized catalyst slurry for return to the top of the regenerator. The exposure of the demetallized catalyst to the heat of the regenera-
tor serves to sulfide and chlorinate catalyst in sequence to said quench chamber, means for supplying gases to and removing gases from said oxygen-
treating chamber, sulfiding chamber and chlorinating chamber to react at an elevated temperature with the metal contaminants on the catalyst, means for contacting said gas-treated catalyst with an aqueous liquid in said quench chamber, automatic temperature sensing means in said quench chamber to control the entrance of said catal-

yst into said quench chamber thereby regulating the flow of catalyst from said chlorinating chamber, means in each of said chlorinating chamber and oxygen-
treating chamber for regulating the bed level of cata-

lyst in said respective chambers by controlling the flow of catalyst to said chambers from the next preceding cham-

ber, whereby a change in the catalyst flow rate from the chlorinating chamber to the quench chamber controls the catalyst bed levels in and total catalyst flow through the said catalyst demetallization chambers.

2. The apparatus of claim 1 wherein a cooling chamber is connected by valved lines for catalyst flow between the sulfiding chamber and chlorinating chamber, said cooling chamber comprising a vertically elongated vessel divided into two flow paths, the first of said flow paths compri-
ing a plurality of heat exchange tubes having a common upper header and a common lower conical chamber di-

vided by a porous plate, said upper header being provided with a solids entry tube leading from outside the vessel and a fluidizing gas outlet tube leading to outside the vessel, said lower header being provided with a porous plate with a solids exit tube leading to outside the vessel, and below the porous plate with a fluidizing gas inlet tube leading from outside the vessel, said second flow path surrounding the said lower conical chamber and each of said plurality of heat exchange tubes and being provided at the bottom with an inlet for cooling fluid and at the top with an outlet for cooling fluid.

3. The apparatus of claim 2 in which means are pro-

vided for the introduction of said cooling fluid responsive to the temperature in said chlorinator.
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4. The apparatus of claim 2 in which the tubes are provided with horizontal fins on their outside.

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