

# Utilization of Industrial Wastes

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The more important of the large number of instances are reviewed where industrial or trade wastes are converted through research into raw materials for the manufacture of commercial products. Differentiation must be made between by-products in the usual sense and materials which are true wastes—not only useless but often involving expense for their satisfactory disposition. Under such classification may be included the manufacture of sulfuric acid and recovery of elemental sulfur from smelter gases, production of sulfuric acid from hydrogen sulfide in petroleum still gases, and recovery of by-product sulfur from hydrogen sulfide in illuminating gas. Sulfite waste liquor has become the source of vanillin and other products.

Waste casein finds its way into resins and adhesives; the fermentation residues in the alcohol industry have been converted into cattle foods and the carbon dioxide into Dry Ice. Potash is recovered from the dusts of the cement industry, and building blocks have been made from fly ash.

In a sense the long list of solvents now recovered from gases derived from petroleum represent success in the use of otherwise waste materials. The same may be said of cements made from blast furnace slag, and synthetic methanol utilizes carbon monoxide present as an interfering substance in gases used in the fixation of nitrogen. Furfural from oat hulls, celotex from bagasse, are other examples.

THIS summary, admittedly incomplete, can provide only a background for more intimate discussions of unsolved problems of disposing of industrial wastes. Much of this summary is reminiscent. For years one of the proudest boasts of chemistry, next to that of devising entirely new products, has been the conversion of materials of little value, particularly wastes, into salable products.

Industry, generally, is organized to manufacture principal products. There may be by-products. New economic conditions and new demands may reverse the importance of the main and the by-product. Too often there is an actual waste material—that is, one for which no demand exists and whose proper disposal may involve considerable expense. The profitable utilization of such an industrial waste is rarely possible. Ordinarily the balance from such an operation is on the wrong side of the books. On the other hand, wastes are the responsibility of the many manufacturers, and their disposal is part of overhead or operating cost. If a return is realized, this may only reduce cost; but if a profit is made, the waste becomes a true by-product. There is an increasing tendency for the community to see to it that the burden of industrial waste disposal is not placed upon the public, and the signs of the times are seen in the establishment of legal guideposts. It is becoming increasingly difficult merely to throw away an industrial waste or to discharge it into a convenient stream. Some wastes cannot even be burned without arousing objection from neighbors.

One of the earliest examples of legislation requiring the conservation of waste was the Alkali Act of 1863 in England. This required alkali works to condense hydrochloric acid gas which up to that time had been allowed to escape into the air. In the Chance process sulfur was recovered from waste produced in the manufacture of sodium carbonate by the Le Blanc process. Until that time mounds of evil-smelling sulfide accumulated near the Le Blanc soda works.

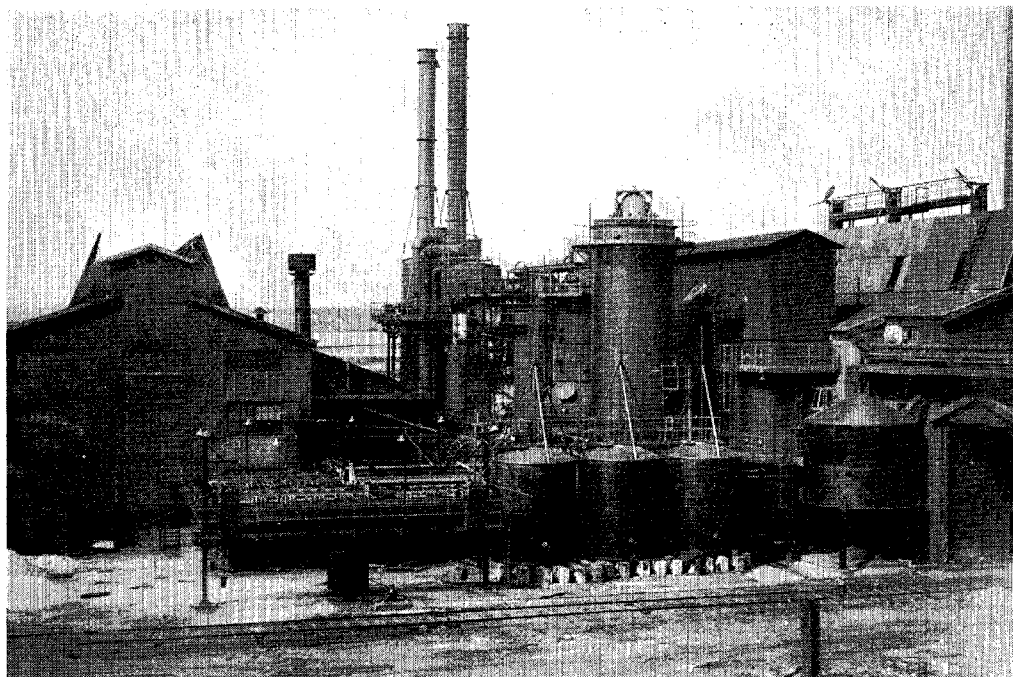
One recalls the application of law, chemistry, biology, and engineering in using the time-honored wastes of the stock-

yards and many ancient stories about them. In a similar category are the practices of the forester and lumberman, reported to do more than the stockyards by utilizing even the bark.

Commercial utilization of cottonseed and its products has become classic, and much of our synthetic organic chemical industry, of which we are justly proud, is based on the utilization of materials that were waste products. The fermentation industry depends almost wholly on the utilization of a waste product of agriculture—blackstrap molasses. At times the demand for this material, together with the more or less successful efforts at cornering the supply, requires its importation from as far away as the island of Mauritius. This may seem strange, for at one time it was difficult to convince the sugar makers of Hawaii that it would be more economical to save by-product molasses than it would be to dump it into the sea.

## Pulp and Paper

Accomplishments in commercial utilization of industrial wastes should encourage those still facing difficult problems. For years a satisfactory disposition of the waste sulfite liquor of the paper industry has been the object of research and development. Of late the preparation of commercial products from this material has been much in the public eye. Years ago in Sweden it was found profitable to produce alcohol on a large scale by fermentation of the sugars in sulfite waste. Similar disposition of the material in the United States is not economical because other raw materials are more desirable. The fact that over 65 per cent of the waste sugars in sulfite liquors are fermentable has led to the creation of bakers' yeast industries in Finland, in Germany, and more recently in Nova Scotia. The plant in Nova Scotia has a reported capacity of over 20,000 pounds a week and is using waste liquor from the newsprint plant of the Mersey Paper Company. Sulfite liquor is the raw material of the Robeson process for the production of a tanning compound, and the adhesive



*Courtesy, Chemical Construction Corporation*

PLANT FOR THE PRODUCTION OF SULFURIC ACID FROM WASTE SULFATE SOLUTIONS

properties of the evaporated liquor are utilized in briquetting powdered fuel, in making core binders, and in road treating agents. One of the adhesives, "Bindex", is well known in the trade. In the West the commercial production of a viscous liquid, containing 39 to 40 per cent solids, from sulfite waste liquor has reached a tonnage in the thousands. More recently an anhydrous product has been made in waste-heat stack dryers and vacuum drum dryers. The product, "Raylig", is used as a road binder adhesive. The liquid or the powder may be dissolved or diluted with water and applied as a soil stabilizer for diminishing dust. It also has a binding action similar to that of other organic materials available for the purpose. One of the largest uses of sulfite waste liquor products is as an adhesive in linoleum cements. This same material, laboratory and field experiments indicate, will be a valuable source of calcium for poultry feeds and a useful spreader for orchard sprays.

The foaming tendency of sulfite liquor has led to its incorporation in small quantities in certain soaps (replacing as much as 40 per cent of fatty acids in certain laundry soaps) and to its use as an ore flotation agent. The lignin of sulfite liquor has been isolated and reduced by certain catalysis, to yield high-boiling compounds which may be of value as solvents. Recently it has been shown that lignin may be used to remove iron from water.

Impressive is the work of Howard (8) in utilizing the sulfite waste liquors of the Marathon Paper Mills Company. The major objective of research was "to supplement the value of the cellulose pulp by realizing on the commercial potentialities of the large tonnage of noncellulosic organic matter in such liquors". The secondary consideration was the reduction of stream pollution. As a result of this development, Marathon is now marketing a variety of products. The sulfite liquor is treated by a three-stage lime precipitation to yield inorganic and organic solid products and a liquid effluent. The inorganic product, resulting from the first lime treatment, is essentially calcium sulfite which is re-used to make fresh cooking acid. The second lime treatment gives a basic calcium

lignin sulfonate which may be burned as fuel or made to yield other products. Without further processing other than drying and grinding, the lignin product is now being used in car-load lots in a material for the manufacture of portland cement, in boiler feed waters, and in ceramics. Alkaline hydrolysis of the lignin products yields vanillin, and more than a third of the vanillin consumed in the United States is now of sulfite origin. The effluent from the vanillin process is treated further and yields various lignin plastic products such as core and surface sheets for laminating, molding compositions, and lignin coating and impregnating resins. The basic calcium lignin sulfonate may be converted into a complete series of lignin sulfonate salts and into free lignin sulfonic acid. Of these the magnesium and sodium salts are being made in tonnage quantities for use in leather tanning, water treatment, and the manufacture of dispersing agents. Thus we see how successful one deliberate research program for the commercial utilization of a waste has been.

From the relief gases of the sulfite process *p*-cymene, sulfur dioxide, and heat are recovered. The sulfur dioxide and heat are re-used. A paint and varnish remover, prepared by mixing *p*-cymene with ethyl alcohol, methanol, and acetone, is in such demand that 750,000 gallons are produced annually.

At one time black liquor from the alkaline process of pulp manufacture was a serious waste. At present this liquor is evaporated and burned to produce heat and to recover its soda. In some mills activated carbon, which is finding considerable use in water treatment, is also made. Indeed, this carbon is of such value that the cooking process of one mill is said to be built around its recovery.

Another by-product of this soda recovery is the lime sludge from the causticizing of the black ash. This lime sludge is either burned to produce quicklime and again used in more causticizing, or is processed to pure calcium carbonate, which is utilized as a filler in the paper or in the production of sulfite cooking liquor. In the kraft or sulfate process, the gases formed during the cooking process contain recoverable turpentine, dimethyl sulfide, and tall oil, all of which

have several commercial outlets. The sulfate liquor from the digesters is concentrated, processed, and returned to the cooking kettles. The turpentine recovered meets government standards, and the tall oil is used in the manufacture of soap. The dimethyl sulfide, a highly odorous, volatile material, is employed as a warning agent in gas lines.

Although waste paper is not a problem of the paper industry, it is a waste of considerable tonnage and one of the raw materials for paper making. De-inked it becomes a part of a large variety of products. In some instances, notably telephone directories, special inks are used to facilitate a de-inking process to be applied later. A sludge results, but thus far no use has been found for it. Much old paper stock finds its way into a number of board products. Broke is, in a sense, a waste product, although it is returned to the paper beaters and re-used.

At one time white water from paper mills was simply run into the sewer, but this created sanitary problems and now many paper mills operate on a closed system or have installed some type of save-all to recover fiber and filler and return the clarified water to the paper machine.

### Wood

The manufacture of tanning materials from chestnut wood yields a considerable volume of waste chips. These have been made the basis of an industry producing a variety of corrugated board. In this same field should be mentioned the extensive research of the Forest Products Laboratories on the utilization of waste wood and sawdust. Some success has come from their efforts to produce a resin from the lignin.

The Weyerhaeuser Timber Company converts waste sawdust into logs by forcing it into tubular molds under considerable pressure; the heat of pressing causes the sawdust to fuse. By the time the mold, which is mounted on a large wheel, has completed a cycle, the fused sawdust has cooled and has been ejected from the mold. The resultant log-shaped product is an excellent fireplace fuel, burning with an even steady heat. Chemicals mixed with the sawdust give various colored flames which make the fuel particularly attractive for holiday use. On occasion, the demand exceeds the supply.

The operations of the Brown Company afford a classic example of waste utilization. Originally the company developed a small waterfall to provide power for a sawmill and later a pulpmill. Since there was an excess of power, sodium hydroxide was produced by electrolysis for use in paper manufacture. The chlorine in excess of that needed for bleaching was utilized to make carbon tetrachloride, and later the waste hydrogen was turned to the hydrogenation of peanut oil. The final step was the acquisition of 25,000 acres of land in Florida for the production of peanuts for oil for hydrogenation. The company also pioneered in the utilization of the black liquor from the sulfate process. Hugh K. Moore was prominently identified with this work.

In 1924 the Ford Motor Company established a complete Stafford-process wood distillation plant at Iron Mountain, in the hardwood forest district of northern Michigan, for

the utilization of wood waste resulting from the manufacture of bodies, truck panels, and packing cases. The gas obtained was burned as fuel, and pyroligneous acid was worked for the usual products while the charcoal was graded, pulverized, and briquetted. Even though motor car construction does not require the amount of wood it formerly did, the waste from the manufacturing of truck bodies and packing cases keeps this plant operating steadily.

How one product from waste makes available another product from waste is illustrated by the practice of a naval stores company which uses pine tree stumps as a source of rosin. By treating the dark-colored wood rosin with gasoline and furfural, a pale rosin of greater value is obtained.

### Pickle Liquor

Pickle liquor has long been a problem in the steel industry. In 1925 a patent was issued to Stevenson covering a process for producing ferrous sulfate from this material, and a plant of the American Rolling Mill Company, at Butler, Penna., is operating under that patent.



BOTTOM OF STAFFORD RETORTS, AND HOGGED SCRAP WOOD ON A RETORT CONVEYOR AT THE FORD WOOD DISTILLATION PLANT, IRON MOUNTAIN, MICH.

The Ferron process is another devised to use waste from steel pickling operations. It is applicable to pickling liquor but not to wash water. It consists of precipitation with lime under controlled pH and temperature to yield a thick slurry. The slurry is filter-pressed, disintegrated, and dried to form Ferron, which is marketed as an insulation and building material.

The volume of pickle liquor is such that the ferrous sulfate made from it is very close to an industrial waste. It has been roasted by acid manufacturers as a raw material for fuming sulfuric acid. There is much interest in the action of copperas on city sewage since the material produces desirable flocculation; it is strongly urged that more city sewage be treated with this material for it has certain important advantages. If this plan is ever widely followed, there would be no surplus ferrous sulfate.

The waste product obtained from tanks in which aluminum sheets are pickled is a sediment containing much alumina and free soda. Formerly thrown away, it is now used in the glass industry. Here it was once necessary to buy pure alumina to put in the mixes which also contained silica and soda.

### Minerals and Metals

Practices in the gold mining industry offer an excellent illustration of how more efficient methods may create new sources of raw materials. Amalgamation made it possible to rework the waste heaps from early gold prospecting methods. Cyanidation methods extracted a profitable amount of this precious metal from the material which had been treated by the amalgamation method. Following this, the technique of flotation, which had worked so profitably on zinc and lead slimes, was used to recover the gold not removed by cyanidation.

For some years the sink-and-float process of mineral separation has been under development by the du Pont Company; following a series of successful demonstrations, the pilot plant has been purchased by an operating company and put into continuous service. Although most of the work has been done on coal, separating this material from slate and other noncombustibles, the process may be highly valuable in other parts of the mining industry in working over waste piles left by other processes.

Tin recovered by the Goldschmidt process has long found its way into the textile industry in the form of the tetrachloride for silk weighting. The textile industry formerly discarded spent tin weighting baths but now recovers the tin content by precipitating as tin hydroxide, which is smelted to metal.

Cadmium is a by-product of zinc smelting. Precious metals are recovered from the sludge of copper refineries. Selenium, now widely used in making ruby-colored glass, was once a waste of copper refineries, and antimonial lead is produced by working up the scum from softening furnaces in lead refining.

Mineral wool is a generic term covering a number of similar products differentiated chiefly by the raw materials from which they are made. Rock wool is made from natural rock or from various combinations of natural minerals. Glass wool is made from silica sand, soda ash, and limestone, with or without scrap glass or other materials. Slag wool represents a commercial use of industrial waste; it is made from iron, copper, or lead blast furnace slag, alone or mixed with flux materials. In 1938 the production of mineral wool is

estimated to have been 400,000 tons, and in 1939 the equivalent of probably 160 cupolas are in operation. There are seventy-one producing companies in the United States operating eighty-two plants.

There have been many attempts to utilize fully blast furnace slag. In 1938 thirty-four companies, operating seventy plants, were engaged in preparing blast furnace slag for the market. This material goes into concrete for roads, paving, and building operations, and is used as railroad ballast and roofing, for sewage trickling filters, in agriculture for its phosphorus content, and as a source of mineral wool. Some of our largest cement works utilize blast furnace slag as one of their raw materials.

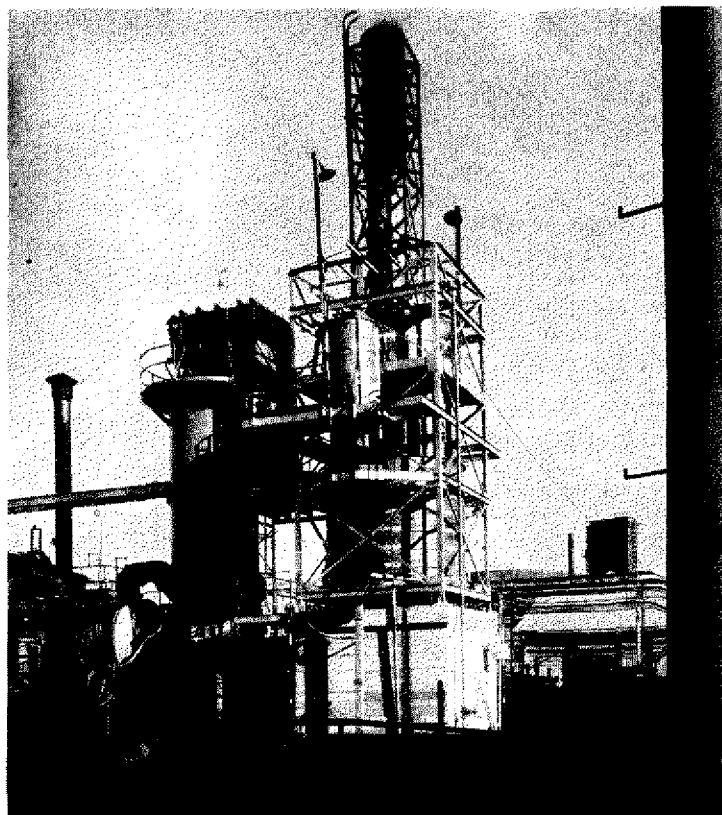
An excellent example of slag utilization is offered by the Eagle Picher Lead Company at Joplin, Mo. During the first years of the depression a process was developed to utilize the material for the manufacture of a specialty insulation. The considerable demand which developed throughout that territory and the oil fields soon reduced the unsightly waste pile.

### Petroleum

The petroleum industry recovers sulfuric acid from the acid operations of oil refineries and, by extraction, sulfonic acids from sludges resulting from such refining operations. The oil-soluble sulfonic acids are used as emulsifying and wetting agents. Naphthenic acids, recovered from certain crudes, are used for heavy metal soaps, for varnish and paint dryers, and in extreme pressure lubricating compounds.

Several processes have been devised for the reclamation of used lubricating oil, although where all costs are considered there is a question as to whether this is always economical.

In a broad sense a material used for a purpose that does not yield the highest return may be regarded as a waste. The



*Courtesy, Western Precipitation Corporation*

ACID MIST COTTRELL PRECIPITATOR

paraffin hydrocarbon gases fall under such a heading, and the waste of natural gas, crude oil distillation gas, and cracked gas has been enormous. On the basis of 1939 production, it has been estimated that there are available in the United States 2500 billion cubic feet of natural gas, and 350 billion cubic feet each of crude oil distillation gas and cracked gas—a huge total of 3200 billion cubic feet. This is probably made up of 2531 billion cubic feet of methane, 36.35 billion of ethane, 159.5 billion of propane, and 96 billion of butane. Some butane is being dehydrogenated into butylenes which, in turn, are polymerized into isooctenes and then hydrogenated to isooctanes for aviation fuel. It may also be processed into butadiene, now of interest as a source of one type of synthetic rubberlike polymer.

Though hydrocarbon gases have been liquefied and widely used as fuel at a profit over similar utilization in the refinery, only when they become raw materials for long lists of solvents and other chemicals, such as those made by the Carbide and Carbon Chemicals Corporation, is their greatest value realized.

Vistanex polybutene, a high-molecular-weight substance useful in rubber compounding, is one of the products made by the dehydrogenation of butane to butylene. Butylene is then polymerized, and the material is available in a range of giant molecules.

The production of amyl alcohol from petane by the Sharples Solvents Company is an achievement in this field. This company formerly stripped pentane from casing-head gasoline, without detriment to the gasoline as fuel, and chlorinated it with gas from a neighboring electrolytic alkali works. The hydrolysis of the chloropentane was carried out with cell liquor, also obtained from the alkali plant without concentration or purification. When the chloropentane had been changed to alcohol, the cell liquor, in which the sodium hydroxide had been reconverted to chloride, was pumped back to the electrolytic cells for another cycle of operation. This company continues to produce amyl compounds from the pentane of casing-head gasoline but now purchases the hydrocarbon.

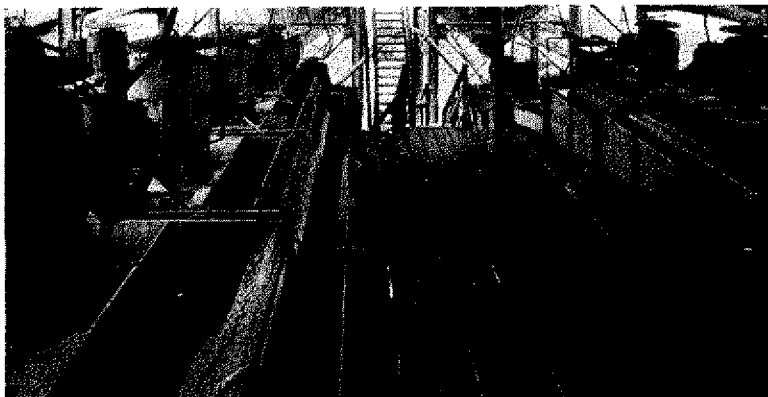
### Gases

The disposition or utilization of sulfur dioxide and trioxide has been a vexing problem. At Trail, British Columbia, the smelter has been required to reduce the sulfur content of its waste gases to a concentration not harmful to vegetation. At Ducktown, Tenn., and Anaconda, Mont., a similar problem has been faced.

A favorite method of utilization where the sulfur content of the gases is high enough, has been the production of sulfuric acid. In some instances, however, this has made the sulfuric acid a waste material, and there have been difficulties in its utilization or disposition. Acidulation of phosphate rock, in the manufacture of some form of phosphate for agriculture, has taken much of it.

At Trail elemental sulfur is being obtained. Powell (16) discusses several methods for the recovery of sulfur from fuel gases, and the literature gives many references to similar activities in Germany where dependence for sulfur is now placed almost wholly in what is recovered from smelter, coke oven, or other gases.

H. F. Johnstone has done a great deal of work on the removal of sulfur dioxide, along with the dust which is also objectionable, from flue gases. As Johnstone pointed out, cleaning waste gases is expensive regardless of the method used,



FLOTATION OF FINE PHOSPHATE ROCK (SANDS) FORMERLY DISCARDED AS A WASTE PRODUCT IN THE SEPARATION OF PHOSPHATE ROCK FROM SILICA SAND AT THE AMERICAN CYANAMID COMPANY'S FLORIDA PHOSPHATE MINES

and even though sulfur dioxide or sulfur in some other form may be sold, it is not to be expected that an actual profit will be realized at present. One must remember that the quantity of material from a single plant is often to be measured in hundreds of tons per day, and it is inconceivable that chemical markets will be able to absorb all of the sulfur which could be produced in this way. Here again public interest may require the cleansing of waste gases, but the products obtained may yet constitute an industrial waste without great possibility of complete commercial utilization.

The Longyear process of Comstock and Westcott for the recovery of sulfur from smelter gases where sulfide ores are processed is planned for operation in Canada, and the potentialities are put at 45,000 tons of sulfur annually.

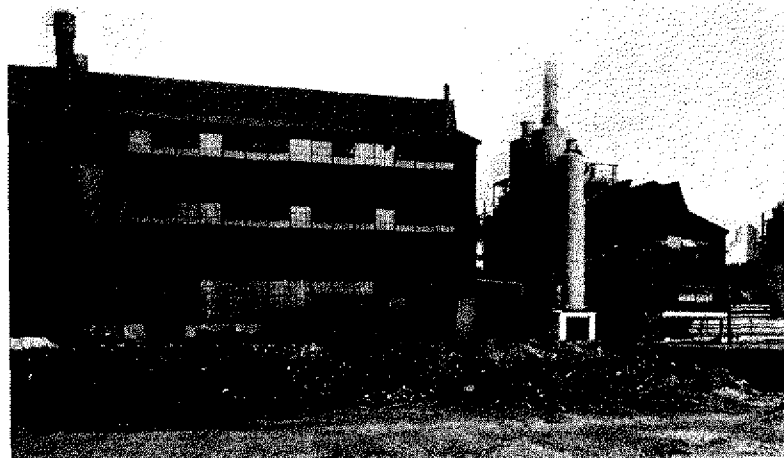
R. V. Kleinschmidt has given particular attention to removal of objectionable materials in flue gases by a wet spray or scrubber. He has found this effective not only in removing sulfur dioxide but also dusts and fly ash which are often objectionable.

The advent of hydrogenation has meant utilization for much of the hydrogen which was formerly a waste of the electrolytic plants. The necessity of removing carbon monoxide from water gas to yield hydrogen for hydrogenation and ammonia synthesis led to the synthesis of methanol.

Dry Ice was originally produced from carbon dioxide manufactured for the purpose. Today at least 85 per cent of our production is made of by-product carbon dioxide from fermentation and other industrial processes.

### Dusts

The various dusts precipitated by the Cottrell method also find a place in industry. The first installation of a Cottrell precipitator, at Riverside, Calif., was made to prevent further damage by cement dust to surrounding vegetation. As a secondary and profitable effect a large amount of cement dust is collected which would otherwise be wasted. The recovery of potash from the flues of cement plants was important during the World War. In other instances dusts of a wide variety are recovered either for their value or to prevent nuisances. One of the most difficult to handle—fly ash—presents a problem in disposal even after recovery. Attempts to utilize it have included its use in artificial stone. At the Royal Mint of Canada, at Ottawa, a Cottrell precipitator was installed to recover various values from fumes. Within a comparatively short time the value of the recovered metal exceeded the original cost of the installation. Practically all the crude arsenic produced in the United States is recovered from lead and copper smelting and gold roasting. Indeed, new



*Courtesy, Chemical Construction Corporation*

**PLANT FOR THE PRODUCTION OF SULFURIC ACID FROM OIL REFINERY SLUDGES**

uses or disposal methods are sorely needed because arsenic, recovered from waste, is becoming a waste.

The clothing has long been supplied to workers in precious-metal refining plants, and when worn out the garments are burned for their metal content. It has even been found economical to filter the air from the refineries for the air-borne metal particles.

The Cellite Company, in order to avoid a serious dust problem, removed and collected the fine particles of diatomaceous earth from the air in its factory. This product subsequently found an outlet as a fine abrasive for silver polish, automobile polish, etc. The demand for the abrasive exceeded the supply, and so a plant had to be erected to produce, on a commercial scale, a product formerly regarded as a waste.

### **Sewage**

In recent years we have seen a successful experiment in the treatment of city sewage at Milwaukee where the adjustment of pH of the tank effluent made possible the filtration of the material. This led to success in preparation of a fertilizer which has had wide distribution and splendid consumer acceptance. The result has been ability to handle a difficult city sewage at much lower cost or even a small profit to the community.

In Germany sewage sludge is being utilized for the fertilization of farm lands and sewer gas as a motor fuel is receiving increased attention. The Department of Commerce reports that Stuttgart has been particularly successful in recovering these waste materials. After several years of pioneering research, the city has been able to recover considerable quantities of clarified sludge which has been taken by farmers for fertilizing purposes; some of it is transported considerable distances in tank cars. This amounted to 6000 cubic meters in 1936, 20,000 in 1937, and 22,000 in 1938. The recovered sewer gas in 1938 was approximately a million cubic meters for use as a motor fuel, estimated as equivalent to a million liters of gasoline.

### **Agricultural Wastes**

We have become familiar with the many problems involved in the effort to use agricultural wastes, and much has already been accomplished. Some years ago Celotex, the wall board from bagasse, made its appearance, to be followed by many other boards from waste materials. Without attempting to name them all we can list Masonite from waste wood, Maftex from extracted licorice root, boards from cornstalks made by

the Sweeney process, and several building boards and insulating blankets made by different units in the lumber industry. In the manufacture of Masonite panels and construction boards from wood waste by exploding, the release of tannic, formic, and acetic acids gives the resulting pulp a pH of 4 or 4.5. Washing with a well water of high sodium carbonate and bicarbonate content, not suitable for boiler use, brings the resulting pulp to the desired pH of 6.5. In the manufacture of Celotex board from bagasse there are wastes which are used. The pith washed out of the fiber is collected and sold to explosives manufacturers, and the dust resulting from fabrication of the board is collected and sold to the plastics industry as molding flour.

Cattlefeed and casein are produced in considerable quantities from surplus milk. The casein is used in the manufacture of paper coating, adhesives, paints, and plastics.

A plant at Laurel, Miss., has been in operation for the past year or two and is producing, on a commercial scale, white starch from sweet potatoes. This provides a domestic source of a starch said to be suitable for adhesives and textiles; it can compete with cassava, which is not grown in this country, and with tapioca, which must be imported. This promises to be the first in a series of similar new industrial enterprises.

In the manufacture of starch from corn, the soluble corn solids from the tailing end of the gluten filter now go back into the process and these utilize a former waste. This process is described in the Widmer patent.

Furfural and its several derivatives are well known. Originally research was directed toward the use of corncobs, but because large quantities of oat hulls were available in one place and were also suitable for furfural production, they, rather than corncobs, became the raw material. Prior to the production of furfural, oat hulls had been used as cattle feed and boiler fuel. Any pentosan-containing material is a potential source of furfural, and several attempts have been made to collect corncobs in sufficient quantities for its commercial production. However, costs were too high and to date oat hulls remain the economic commercial source. Various estimates place annual consumption of furfural at about 6,000,000 pounds, made from about 10 per cent of the oat hulls available in the United States.

The use of soybean meal in the manufacture of plastic parts, particularly for automobiles, is another instance of agricultural wastes becoming important as commercial raw materials.

The shells which remain after cashew meats have been extracted from the nuts have been made the source of an oil which serves as a raw material for a superior insulating varnish. The oil is boiled with amyl chloride, and the resulting material is used in cable insulation. A polymerized product of the cashew shell oil is utilized in brake linings. Last year more than 3 million pounds of cashew shell oil were imported, and the number of products made from it is now extensive, ranging from cable insulation to liners for bottle caps. With the amyl chloride used in this process and obtained from pentane formerly wasted in casing-head gasoline, we have here a commercial product made on a large scale through utilization of two industrial wastes.

By-products manufactured from citrus fruits, which because of size, shape, ripeness, or surplus were long regarded as a waste, is another of our classic examples. From lemons have come citric acid, lemon oil, and pectin; and from oranges we obtain juices, oil, marmalade, and pectins, with the pulp

going into cattle feed. The avoidance of waste incident to shipping the whole orange great distances only to be juiced at the journey's end continues a subject of research. Some canned or bottled orange juice acceptable to the market has been produced, but it may still be regarded as one of the problems of the industry.

Lately the banana industry has conducted experiments with shredded banana stems, now a waste in producing countries because of the practice of packaging the fruit instead of distributing it in bunches as was the former custom. These shredded stems provided a satisfactory mulch which within a year disintegrates and supplies humus to the soil.

Nicotine sulfate, so largely used in insecticides, is produced from the waste parts of tobacco plants, particularly stems and the midribs of leaves. This material would otherwise be used only as a mulch.

Beet molasses is a complex material, and from it there have been prepared methylamines, ammonium sulfate, sodium and potassium cyanide, various potassium and sodium salts, and a variety of organic acids and esters. Molasses would represent considerable waste were it not for the use of osmosis and the Steffens process. The problem has not been completely solved because the Steffens process gives rise to another waste, from some of which glutamic acid and betain are made in commercial quantities. The molasses is also used for yeast cultivation, for cattle feed, and for alcohol manufacture.

Cotton linters may also be regarded as an industrial waste, for prior to the World War there was no use for them. However, when cellulose was badly needed for munitions, linters were recovered. This practice has continued although the principal product is no longer munitions but cellulose acetate. From cottonseed, once a great waste, an immense number of valuable products have been obtained; the latest is a sweeping compound from the hulls. The press cake from the manufacture of linseed, soybean, and cottonseed oils is used in cattle feed.

### Miscellaneous

In the days when the packing houses in Chicago discharged their wastes into Bubbly Creek, where they mixed with raw sewage and dilution water pumped from Lake Michigan, the grease separated and rose to the surface when the waste met the cold lake water. Thrifty scavengers placed a raft near the sewer and recovered the floating fats, making as much as a hundred dollars a day from this source. The packers soon put a stop to their own wastefulness by installing grease-collecting basins in the plants. Medicinal products are produced from the glands and livers removed from slaughtered animals in the latest step toward complete use of packing-house wastes. Animal hoofs and horns are employed in the manufacture of glue.

Distillers' grains, the solids from distillation, have long been used as stock feed, but only a few of the larger distilleries practice complete recovery of their slops. Some of the wastes, such as those from the yeast plant, are too dilute to justify recovery for feed purposes but cause serious pollution of streams into which they may drain. Evaporation of thin slop and the addition of the resulting sirup to the regular distillery grains has been found uneconomical; but where the liquid is pretreated to permit multiple-effect evaporation to a high solid content, this recovery is made profitable. The method employed by Hiram Walker & Sons, Inc., which involves the use of centrifugals, appears to be practical.



*Courtesy, Dorr Company*

THICKENER RECOVERING FINE RUBBER STOCK AT THE RUBBER RECLAIMING PLANT OF THE GOODYEAR TIRE & RUBBER COMPANY AT AKRON

In the wool industry recovery methods such as acid cracking, solvent extraction, aeration processes, and centrifugal methods are practiced in removing lanolin from scouring wastes. The grease may be distilled for its oleins and stearins for use in the manufacture of soap or used as oils. There is some demand for it as a leather dressing, and refined lanolin is valuable in cosmetics and certain pharmaceutical preparations. Apparently the most convenient present method of degreasing wool is solvent extraction with such solvents as naphtha or chlorinated hydrocarbons. After extraction the solution is distilled and the grease recovered. A new method of freezing wool, urged by some, may eliminate much of the waste of some processes, since at low temperatures from 30 to 90 per cent of the original grease in the wool can be removed by beating before it goes to a scouring bath.

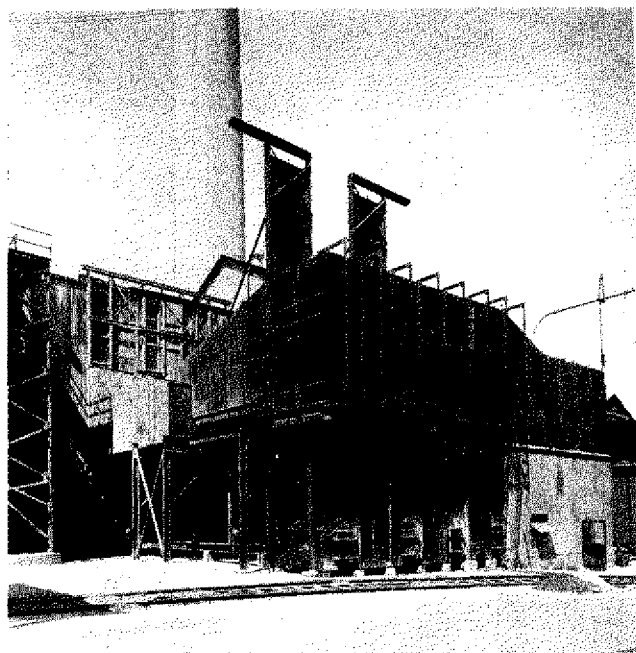
In the fishing industry there was formerly great waste inasmuch as the fillets represent only 40 per cent of the eviscerated fish. The backbone, head, skin, fins, etc., are now utilized for the manufacture of fish meal, glue, and other by-products. Formerly this waste could not be merely thrown away but at considerable cost was transported to sea and dumped. Today the bones and skin are cooked for several hours to glue, and the scrap is pressed and dried for use as feed or fertilizer.

The Koppers Company has developed a method for removing phenol from ammonia still wastes. After the free ammonia has been distilled and before the fixed ammonia is removed, the still waste is pumped to the top of a packed tower which is divided into two sections. The bottom section contains jets which spray 10 per cent caustic solution through a rising hot vapor, mostly steam. After passing through this spray and being dephenolized, the vapor enters the top section of the tower and meets the descending spray of fixed ammonia liquor. The vapor absorbs the phenols contained in the still liquor and is recirculated to the caustic spray section for dephenolization and another cycle. The ammonia liquors are continually withdrawn, and the phenol is recovered from the caustic liquor.

The experience of Commercial Solvents Corporation is a matter of history. During the World War low-grade corn was used to produce acetone and ethanol by fermentation, the waste products being butyl alcohol, hydrogen, and carbon dioxide. Later the butyl alcohol was made into butyl acetate for the first of the new lacquers and became the tail that wagged the dog. The carbon dioxide is now sold in the form of Dry Ice. More recently this same corporation has been active in the nitration of paraffins using natural gas as one

of the basic raw materials. A new technique has produced a nitromethane, nitroethane, and similar compounds from which a variety of chemicals are being made. The nitroparaffins are direct and active solvents for nitrocellulose, for a wide range of synthetic and natural resins, for fats, and for some dyes. Some of the members of the new group show antigelling properties, an advantage useful in rubber cements; nitroethane brings about such gelling in rubber latex.

Spent soap from textile plants was formerly discharged into the sewer. Now oleic acid is obtained from the waste soap solutions by various recovery processes. Glycerol is a valued product from the manufacture of soap.



Courtesy, Western Precipitation Corporation.  
POTASH BY-PRODUCT RECOVERY SYSTEM AT A CEMENT PLANT;  
THE COTTRELL IS PRECEDED BY MULTICYCLONE MECHANICAL  
COLLECTORS

In the manufacture of chamois leather, the excess of partially oxidized cod oil, drained and squeezed from the leather after the soaking period, is valuable commercially as an emulsifying oil. The oil now used in the chamois leather manufacture is largely a by-product of vitamin extraction operations.

Coumarone resins are made from high-boiling coal-tar products which were formerly wasted. Millions of pounds of these resins are sold yearly for use in printing ink, as a binder for floor tile, and even as a constituent of chewing gum.

Cinders are widely used with cement, as in cinder building blocks; and to the Rumford Chemical Company goes credit for perfecting a building block from waste calcium sulfate. The American Cyanamid Company uses its waste calcium sulfate, a by-product of phosphoric acid manufacture, for the manufacture of several types of gypsum building products and gypsum wall plaster.

Waste brines of the West Coast have been made to give up their iodine content and thus enable the United States to be independent as regards a supply of this element.

We must not overlook the extensive use of reclaimed materials known as junk. This reclamation is the basis for several large operations such as those of the Western Electric Company where the values handled annually approach 10,-000,000 dollars and require the services of some ninety to a hundred employees. To regain values with minimum loss and

to rework the recovered materials into the form required calls for expert metallurgy. No. 1 scrap cast iron will yield about 96 per cent of new cast iron, stove plate 90 per cent usable new iron, and heavy milling steel scrap 95 per cent new steel. Zinc is recovered to the extent of 75 per cent of the stock charged, and many other metal products are recovered and re-used.

Such used rubber tires as can be economically collected provide the raw material for rubber reclaiming plants, and some tire cuttings may reappear in the form of door mats and certain types of roofing materials.

### Conclusions

One difficulty was ever present in the preparation of this paper—the determination of “waste”. One generation of chemists spoke of the utilization of “waste cottonseed”, “waste products from coke plants”, and the wonderful utilization of the waste gases from the Ducktown smelters for the manufacture of sulfuric acid. We may no longer consider the industries that have grown from such ventures as illustrations suitable for our topic. At one time they might have been but not now. The examples given here will some day be considered established practices and not extraordinary in any sense. So be it. It will mean only that chemists have advanced further toward an efficient utilization of wastes. It can mean only that there will be new problems in the utilization of some product for which a use or a market has not yet been found. This is our definition of waste.

Earlier in this review we referred to the British Alkali Act, the purpose of which was to abate a nuisance. In the beginning it was a thorn in the flesh of the alkali manufacturers. Later it became a vital factor in building not only the British chemical but the British textile industry as well.

In this country much has been accomplished without benefit of legal compulsion—for example, the rapid growth of synthesis from waste petroleum gases; but much remains to be done with wastes, some of which cause actual nuisances. In eliminating them the force of law may lead to profitable exploitation and, although intended to lead to nuisance abatement, may in fact help establish important industries.

### Bibliography

- (1) Bartow, E., and Walker, W. W., *IND. ENG. CHEM.*, **30**, 300 (1938).
- (2) Boehm, R. M., *Trans. Am. Inst. Chem. Engrs.*, **25**, 219 (1931).
- (3) *Chem. & Met. Eng.*, **38**, No. 9 (Sept., 1931).
- (4) Edwards, R. S., *Trans. Am. Inst. Chem. Engrs.*, **16**, Part 2, 39 (1924).
- (5) Eweson, E. W., *Chem. Industries*, **38**, 573 (1936).
- (6) Frolich, P. K., *IND. ENG. CHEM.*, **30**, 916 (1938).
- (7) Geyer, J. C., *Sewage Works J.*, **9**, 625 (1937).
- (8) Howard, G. C., *IND. ENG. CHEM.*, **22**, 1184 (1930); **26**, 614 (1934).
- (9) Kershaw, J. B. C., “Recovery and Use of Industrial and Other Wastes”, London, Ernest Benn, 1928.
- (10) Kobe, K. A., Layman, J. H., and Armbruster, F. R., *IND. ENG. CHEM.*, **28**, 571 (1936).
- (11) McElhinney, T. R., Becker, B. M., and Jacobs, P. B., *Ibid.*, **30**, 697 (1938).
- (12) Mohlman, F. W., and Beck, A. J., *Ibid.*, **21**, 205; Snell, F. D., *Ibid.*, **21**, 210; Faies, A. L., *Ibid.*, **21**, 216; Warrick, **21**, 261 (1929).
- (13) Nelson, W. G., *Ibid.*, **22**, 312 (1930).
- (14) Penna, Dept. of Health, “Treatment of Tannery Wastes”, Dec., 1930.
- (15) Peters, F. N., *IND. ENG. CHEM.*, **28**, 571 (1936); **31**, 178 (1939); *Ibid.*, News Ed., **15**, 269 (1937).
- (16) Powell, A. R., *IND. ENG. CHEM.*, **31**, 789 (1939).
- (17) Schmidt, W. A., *Trans. Am. Inst. Chem. Engrs.*, **21**, 11 (1928).
- (18) Teeple, J. E., *IND. ENG. CHEM.*, **18**, 1187 (1926).
- (19) *Trans. Am. Inst. Chem. Engrs.*, **16**, Part 1 (1924); **21**, 1-122 (1928).
- (20) *Trans. Inst. Chem. Engrs. (London)*, **8** (1930).
- (21) Veitch, F. P., and Benedict, L. C., *Trans. Am. Inst. Chem. Engrs.*, **16**, 259 (1924).