Industrial Wastes . . .

ACID MINE DRAINAGE

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▶ ▶ Although many mines discharge alkaline water, the waste water from most of them contains 100 to 50,000 p.p.m. of acid as H_2SO_4. The acid is produced by the action of air and water upon sulfur compounds, mainly iron sulfide, in the coal or adjoining rocks; the result is the formation of sulfuric acid and iron sulfates, frequently associated with aluminum and manganese sulfates. Certain chemical reactions, which give as end products free sulfuric acid and basic iron sulfates and hydroxide, are well recognized; but there is too little knowledge concerning the intermittent reactions and the factors, including possibly bacterial action, which govern the rate of acid formation or its inhibition, and which may hold the solution to the pollution problem and explain many anomalies. The strongest acid comes from the old workings and persists for years. Research now under way is promising. Trapped sealing of abandoned mines to exclude entrance of air while permitting outflow of water is the most effective present means of reducing pollution. Covering of sulfur-bearing waste material and exposed coal faces in strip mining operations with consolidated material to exclude air and water is important. There is an insidious lag between exposure of coal and appearance of acid. In addition to acid drainage, silt (mainly from anthracite breakers) has been an inert but gross pollutant, but this is now being put under effective control.

ACID coal mine drainage is an industrial waste which is peculiar in that it arises, not from the processing of the coal, but as a result of the mere extraction of the mineral from the ground. It has caused gross and widespread pollution of the streams in and below the coal fields of the country, particularly the Appalachian field; were it not for the fact that there has been no recognized practical means for preventing this waste, it would never have been tolerated. The havoc caused by the drainage has been accepted as a necessary and unavoidable evil connected with the essential work of producing that prime requisite of modern civilization, coal. In addition to acid pollution there is also, principally in the anthracite fields of eastern Pennsylvania, pollution by the fine particles of coal and rock refuse (known as silt) which issues from the wet coal preparation plants in the anthracite region and, to some extent, in the bituminous fields.

Lest the seriousness of this pollution and the relation it bears to industry in general be underestimated, let it be remembered that the coal reserves of this country underlie hundreds of thousands of square miles, and the actively worked fields, thousands of square miles; that in 1944 there were mined in this country 620,000,000 net tons of bituminous coal and 63,701,350 net tons of anthracite (*7*); that 460,600 persons were employed in mining this coal, in addition to thousands of others engaged in providing the industry with supplies, equipment, and services. The value of this coal was more than 2.7 times that of all the gold, silver, copper, lead, zinc, and other metals, except iron and iron ore, produced in this country, and this coal produced 54.5% of the kilowatt-hours of energy in that year (assuming "constant value" of water power/coal equivalent). It is evident, then, not only that this industry exerts a profound effect upon our whole national economy but that anything which vitally affects the cost or manner of operating that industry, in turn, similarly affects the whole country.

Although many coal mines discharge alkaline water, from most of them there issues acid-impregnated mine water. The volume of these acid waters is unknown. However, Herndon and Hodge (*3*) estimated that in 1932 the acid drainage discharged from the mines of West Virginia alone amounted to an average of 168,349,000 gallons a day. It is evident that the total volume from the coal fields is enormous. Estimates of the amount of water "made" by a mine vary greatly, from about 350 to 2000 or more gallons per day per acre of mined-out area, with 1000 gallons as a probable average. This drainage varies from mine to mine, depending upon the imperviousness of roof, depth of cover, proximity to springs and water courses, etc., and weather conditions, although the fluctuations in drainage are generally much less than those in the natural flows in the streams.

ACID CONCENTRATION

However, the rate of acid formation does not vary thus, but is more constant. The result is that, during the higher stream stages of the wetter periods of the year, the concentration of the acid in the stream is less, and in some cases the streams may become alkaline; conversely, during the low flow periods of the year the concentration of the acid becomes greater, and streams which are normally alkaline may become acid.

Although the total volume of acid mine waters is not known, an idea of the magnitude of the pollution can be gathered from some estimates of the tonnages of acid discharged annually to some of the principal streams which drain portions of our great Appalachian coal fields. Thus, Hodge (*4*) estimated that over 2,875,000 pounds a day (525,000 tons a year) of 100% sulfuric acid were poured into the rivers of West Virginia during 1934.

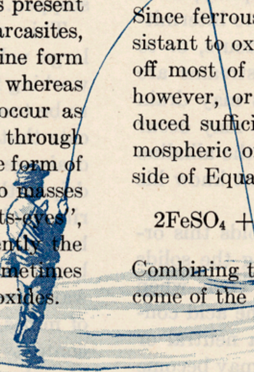
Estimates made during the mine sealing work done by the Pennsylvania Department of Health under the federal W.P.A. program (*5*) indicated that approximately 1,075,000 tons a year of acid were still discharging to the streams in 1938 from the mines in the twenty-six bituminous coal producing counties in that commonwealth after a reduction of 177,000 tons a year had been effected by mine sealing. According to a report (*8*) by the U. S. Public Health Service, U. S. Army Engineers, and cooperating State Health Departments, the Ohio River, including its tributaries in West Virginia and Pennsylvania, received, prior to the start of the mine sealing program, 2,500,000 tons a year of sulfuric acid. Of this amount, 47.4% was credited to abandoned mines, 7.2% to marginal mines, and 44.75% to active mines.

The concentration of the acid varies widely, from less than 100 to nearly 50,000 parts per million with typical values of perhaps about 100 to 6000 p.p.m. as sulfuric acid, with about 10 to 1500 p.p.m. of iron sulfate, 0 to about 350 p.p.m. of aluminum sulfate, and 0 to about 250 p.p.m. manganese sulfate (the latter three reported as the oxides). Mine drainage presents numerous anomalies, and the acidity of the drainage cannot be predicted with certainty. Thus Carpenter and Herndon (*2*) reported on the drainage from two West Virginia mines in the same vein (the Sewickley), within a few miles of each other. The drainage from the mine whose coal ran 3.0% in sulfur had an alkalinity of 170 p.p.m. and amounted to 200,000 gallons per day; the mine whose coal had 2.6% sulfur discharged 130,000 gallons per day of water having an acidity of 30,000 p.p.m.

Outlet Works of a Mine Seal

SOURCE OF ACID

The acid in the mine waters comes from the sulfur bodies in or associated with the coal measures. A small amount of the sulfur may be present as calcium and aluminum sulfate and also, at times, as organic sulfur resulting probably from the degradation of the proteins in the original vegetable matter from which the coal was formed. However, by far most of the sulfur is present as iron sulfide (FeS_2), either in the form of pyrites or marcasites, which are chemically the same but different in crystalline form and ease of oxidation. Pyrite oxidizes slowly, in general, whereas marcasite oxidizes much more readily. The crystals occur as minute particles, usually spheroidal in shape, scattered through the coal, in partings, and in the floor and roof rock, in the form of "sulfur balls" (varying in size from small particles up to masses several feet in diameter), as streaks or veins called "cats-eyes", and as lens-shaped masses of lenticular pyrite. Frequently the sulfur is most concentrated in the floor and roof rock; sometimes the sulfur has been partially oxidized to sulfates or hydroxides.



COURTESY, PENNSYLVANIA DEPARTMENT OF HEALTH

Recovering Fine Coal from Streams below the Anthracite Colleries

Until the coal seam is opened and the sulfur forms are exposed to air and water, acid is not formed. After exposure, the sulfur oxidizes and results in the formation of ferrous sulfate (copperas) and sulfuric acid according to the equation:

$$2FeS_2 + 7O_2 + 2H_2O \longrightarrow 2FeSO_4 + 2H_2SO_4 \quad (1)$$

Since ferrous sulfate in the presence of sulfuric acid is fairly resistant to oxidation, the leaching action of the mine water carries off most of the iron and sulfur in these forms. After a time, however, or when the actual acid concentration has been reduced sufficiently by dilution, there is further oxidation by atmospheric oxygen, and from the components of the right-hand side of Equation 1 we obtain:

$$2FeSO_4 + O + 2H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + H_2O + H_2SO_4 \quad (2)$$

Combining the two reactions in order to determine the final outcome of the oxidation,

$$4FeS_2 + 15O_2 + 2H_2O \longrightarrow 2Fe_2(SO_4)_3 + 2H_2SO_4 \quad (3)$$

In other words, not only do we obtain acid-producing ferric sulfate, but an excess of sulfuric acid at the same time. Finally, when other entering streams bring the acid concentration down sufficiently, the ferric sulfate in turn hydrolyzes,

$$Fe_2(SO_4)_3 + 6H_2O \longrightarrow 2Fe(OH)_3 + 3H_2SO_4 \quad (4)$$

so that finally all of the sulfur, at first bound in insoluble fashion with the iron, is now in the stream as free sulfuric acid.

The foregoing description of the conversion of the iron sulfide in the coal to free sulfuric acid and iron hydroxide in the stream tells the beginning and end of the process and certain accepted steps in the process, but it is far from telling the whole story or explaining the many anomalies exhibited by mine drainage. We need to know much more about the mechanism of acid formation, the intermediate steps between those indicated, and the factors that influence the rate of acid formation. Therein may lie the answer to the prevention or control of the coal mine acid problem.

For instance, it has been suggested, with some experimental proof, that the original iron sulfide oxidizes in two stages:

$$FeS_2 + 3O_2 \longrightarrow FeSO_4 + SO_2 \qquad (5)$$

$$2SO_2 + O_2 + 2H_2O \longrightarrow 2H_2SO_4 \qquad (6)$$

The $FeSO_4$ of Equation 5, of course, follows the reaction given in Equation 2. According to this theory the rate of acid formation is supposed to depend upon the reaction of Equation 5, which is believed to take place very slowly as compared with the reaction of Equation 6. Experiments by Carpenter and Herndon (*2*) led them to believe that bacterial activity also plays a role in acid formation, and recent experiments emphasize this.

Whatever the mechanism of acid formation, the net result is free sulfuric acid, objectionable quantities of basic iron sulfates and ferric hydroxide, and, frequently, troublesome quantities of manganese and aluminum in the stream. The sulfuric acid, which is colorless, renders the water hard; in sufficient quantity it kills all aquatic life in the steam, makes the water corrosive to steel river craft and such river structures as lock gates, and renders it unfit for stock watering purposes and expensive or impossible to treat for public or industrial water supplies.

Where water supplies are purified by slow sand filters, the situation is particularly difficult during rapidly changing stream stages. Unless the varying acidity is promptly corrected by the proper dosages of neutralizing chemical (usually soda ash), there is danger that the bacterial film of the filter, upon which the safety of the water depends, will be destroyed. This is especially true when the character of the stream water changes rapidly, as is frequently the case. The change may be due either to intermittent pumping, especially during off-peak pumping hours, or to variations in stream stages, especially where the streams are formed from tributaries. Some of these tributaries may drain mining areas and some may be alkaline, or rainfall may occur over the basins of the acid tributaries and not over the alkaline areas, or vice versa. Then the waterworks man must know his streams and act quickly and correctly.

If the stream also receives domestic sewage, it holds this organic matter without biological action, often leaving the solids mixed with other sediment on the stream bed. Then when freshets occur or when, farther along in its course, the acid concentration is sufficiently reduced by dilution with a neutral or alkaline stream, bacteriostasis ceases and the stream may become little more than an open running septic tank.

The iron sulfates and the hydroxide give the water of the stream and the banks and bed of the stream the typical "acid mine water" color, which ranges from yellow through orange red to reddish brown. In the vicinity of the mines these sulfates (or "yellow boy") and the hydroxide may even be sufficient in amount to form substantial sludge deposits.

CORRECTIVE MEASURES

Thus far there has been no recognized practical method of treating acid mine drainage pollution in this country or in any other country where conditions are comparable. It is easy enough to neutralize the acid mine drainage in a test tube, and it has often been urged that the mine waters be treated with quicklime, calcium hydroxide, or limestone. This can be done if provision is made for removing the calcium sulfate as it forms; otherwise the sulfate will coat over the lime and stop its action. However, for each ton of coal mined in Pennsylvania, for instance, an average of about 10 tons of water must be disposed of; it is evident that operating costs, exclusive of the capital costs of treatment works, would place a substantial additional cost on each ton of coal produced. Estimates of these costs vary, but in the aggregate they would be very great and would probably be passed on to the consumer.

It has been argued that useful by-products could be secured which would really result in a profit from the treatment; experiments at the Calumet Mine of the H. C. Frick Coke Company have been cited as proof. However, the best information available concerning these experiments indicates that such "profits" as were realized were possible only because of the abnormal conditions of the World War I period; that general application of the plan of treatment would glut and destroy any market for the by-products; and that the experiment was terminated largely because of the problem of disposal of the large volume of sludge produced, which was "too thick to pump and too thin to shovel".

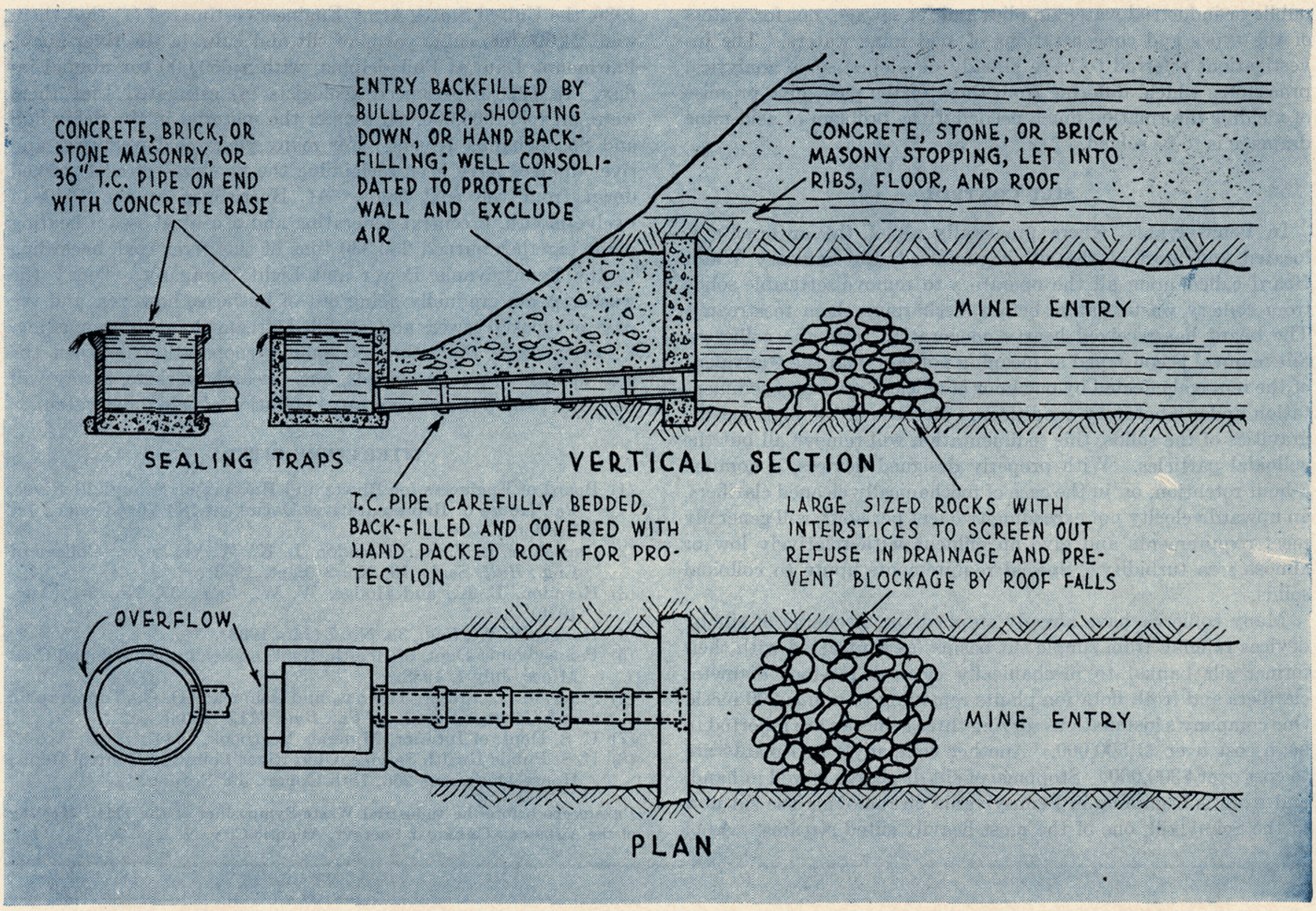
Even if neutralization with calcium were economically feasible, there would still result a highly mineralized water with its hardness in the form of the permanent hardness of calcium sulfate. This water would be unsuited for public water supply without softening and, in many cases, unfit for steam raising or other industrial uses. Even though subsequently softened at additional expense, such water might cause trouble in steaming equipment or in industrial processes because of its high dissolved-solids content. The one present method which offers hope is the "sealing" of abandoned mines.

Sealing consists in closing all openings, such as shafts, portals, outcrops, surface breaks, crop holes, etc., in such a way as to prevent air from entering the mine while, at the same time, providing a trapped outlet, much like a running trap on a drain line, through which water may escape without building up a hydrostatic head within the mine. In this manner, by excluding the one controllable factor (air) of the three (air, water, and sulfur) which produce the acid, its formation can often be minimized or stopped.

This method cannot be applied to active workings because large volumes of fresh air must be constantly supplied to the working faces for the safety of the miners. This may not prove to be too serious a matter, however, for there is evidence to indicate that the water from active workings which does not include drainage from abandoned workings is generally nonacid. Roof drips—that is, the water entering the mine through the roof, the ribs, and the coal faces—have been found to be alkaline with carbonates and bicarbonates of the basic metals and dissolved carbon dioxide. The theory has been advanced that the acid mine waters are really formed in the abandoned or worked-out portions of mines, and that the high carbon dioxide and deficient oxygen contents of the air in these workings are the result of the release of carbon dioxide and utilization of oxygen in the process of converting the sulfur bodies to acid and acid salts under the peculiar conditions of limited air, humidity, temperature, and other conditions existing in these workings. The veteran investigator, R. D. Leitch of the U. S. Bureau of Mines, says that "old worked-out sections of a mine are invariably the source of the most acid water", and unsealed worked-out areas after many years still discharge acid water. However, it is hoped that mine sealing can be applied to some of the mined-out areas of active mines as well as to abandoned mines. This does, however, involve problems of mining laws, prevention of the formation of explosive mixtures in "gassy" mines, and other practical questions, including economics. But the success which has attended mine sealing makes this the most promising method now available.

Other remedies proposed to minimize the effects of acid mine drainage include multiple-use dams to increase dry weather flows and the diversion of acid drainage from clean to already polluted streams. This latter step has been provided for by recent legislation in Pennsylvania to protect, at state expense and under certain conditions, streams which were "clean" on January 1, 1944. The one method is a partial cure; the other, a plan to save some streams at the expense of still greater pollution of others. Both are useful palliatives to serve until a real solution is found.

A special type of sealing appears to offer the most protection at present from that increasingly prevalent form of mining,



One Form of Typical Mine Seal, to Exclude Inflow of Fresh Air While Permitting Free Discharge of Mine Drainage

"strip" or open-pit mining. If streams are to be protected, then the sulfur-bearing refuse, coal, bone, etc., called variously rider, blossom, and rooster coal, should be segregated and covered over with selected material, well compacted and graded to shed rainfall and minimize the percolation of water and air through it. Also, the exposed coal face or "high wall" should be back-filled to exclude air reaching the coal in so far as practical. Another method is to form lakes in the pits with proper protection against washouts, and, by drowning out the exposed coal, to stop its oxidation. The danger from stripping operations lies in part in the insidious time lag between the mining and the appearance of acid drainage, as in the McDonald Water Company case.

The next most important step is *to find a practical cure for the ills of acid mine drainage.* Although many thousands of analyses of mine drainage have been made, much of this information cannot be satisfactorily correlated with the controlling factors because of the various methods of analysis. Much remains to be done to determine the precise mechanism of acid formation, the intermediate reactions involved, the factors which accelerate or retard acid formation, the possible effects of catalysts and of trace elements, and the effects of concentrations of acid and mineral salts. There is a marked difference in behavior between natural acid mine drainage and synthetic waters made up to be presumably identical with such drainage, oxidation being much slower in the latter water. However, when an oxidizing agent such as hydrogen peroxide (H_2O_2) is added to the synthetic water or when the synthetic water is inoculated with natural mine drainage, the normal oxidation changes are greatly accelerated. This fact and the fact that some forms of bacteria are recovered from mine waters give added force to the possible role of bacteria in the production of acid mine water.

Fortunately, fundamental research is going forward at the present time. The State Health Department and the Sanitary Water Board of Pennsylvania have two fellowships in operation at the Mellon Institute for Industrial Research in Pittsburgh, Pa. One of these deals with the effect of acid mine drainage on sewage and the other wastes discharged to streams, and the larger fellowship deals with the major problem of the mechanism of, and the means for minimizing or preventing, the formation of acid mine water.

It has been found necessary to go back to fundamentals and to *undertake a study of the reactions of the pure chemicals* in various concentrations. By laboratory studies with controlled factors and by field studies of actual mine conditions, it is hoped that some new and fundamental concepts may be established whereby the anomalies of mine drainage may be explained and satisfactory analytical procedures developed.

For some years past Bituminous Coal Research, Inc., has also been conducting active research on the fundamental problems of acid mine waters at the Engineering Experiment Station at West Virginia University and has done valuable work in determining acceptable field and laboratory analytical procedures, and investigating various hypotheses. This work by the coal industry itself is an excellent effort to meet a responsibility to public interests, but a greater allotment of funds would speed the work.

Analyses in the past have been based largely upon those given in "Standard Methods for Water and Sewerage Analyses", but these methods were intended primarily for waters suitable for public or industrial water supplies and for sewage, not for waters of the types and concentrations of acid mine waters. The investigations referred to have already developed some analytical procedures which, differing from those of the past, give promise of yielding information much needed if the problem of acid mine drainage is to be solved.

SILT CONTROL

In Pennsylvania, where practically all of the anthracite is located and most of the silt is produced, the Sanitary Water Board called upon all the operators to remove settleable solids from colliery waste waters before discharging them to streams. The board has received hearty cooperation from the collieries. Silt removal is construed as meaning not less than the equivalent of the removal effected by one hour of efficient quiescent sedimentation under laboratory conditions. Because of the high specific gravities of the solids, this sedimentation will remove all but the colloidal particles. With properly designed devices, a nominal 3-hour retention, or, in the case of mechanically cleaned clarifiers, an upward velocity not exceeding two feet per hour, will generally meet requirements and give an effluent with relatively low or almost zero turbidity. Special requirements apply to colloidal solids.

Many collieries have already stopped the discharge of silt by devices ranging from simple silt basins (as contrasted with their former silt banks) to mechanically cleaned 180-foot diameter clarifiers and froth flotation plants removing to minus 200 mesh. One company's installations serving three collieries are reported to have cost over $1,500,000. Another company's two plants are to cost over $300,000. Stoppage of silt discharge is well in hand, and work is beginning in Pennsylvania on removing the silt now in the Schuylkill, one of the most heavily silted streams. As of 1936, the United States Army Engineers estimated (*1*) that there were 24,000,000 cubic yards of silt and culm in the river above Fairmount Dam at Philadelphia, with a 650,000 ton annual influx. In 1926 experienced geologists (*6*) estimated that there were, all told, 900,000,000 tons of the material in the Schuylkill and Susquehanna Rivers. For many years coal washeries and river dredges have been reclaiming the fine sizes of coal washed down from the coal fields. At Harrisburg in the 1943–44 twelve-month, a central generating and a central steam heating plant together burned 230,330 tons of this river coal, according to the Pennsylvania Power and Light Company. Today the washeries are gradually going out of business, however, and the days of blocked sewers and silt-filled stream channels are passing.

Let us hope that, through similar cooperation between the coal operators, public officials, and research workers, a way will be found to stop the present gross pollution of acid mine waters.

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Industrial Wastes . . .

COAL WASHERY PLANTS

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ANTHRACITE has been mined in Pennsylvania for over one hundred years. The industry has increased in size until the annual production was approximately 56,000,000 tons in 1946. Incident with the mining and preparation of anthracite for market, much undersized fine coal for which there has been no market is produced and has to be discarded. In addition to this unmarketable fine coal, considerable tonnages of reject material become mixed with the raw coal in the mining operation and must be brought to the surface. After separation from the coal this reject material must be stored on rock banks. The disposal of these waste materials has become a serious problem in the anthracite region, since much of the coal occurs in narrow valleys which have become congested by the mining operations and the towns.

Large amounts of both the unmarketable finer-sized coal and refuse rock have accumulated near the mining operations. As a result of the shortage of disposal areas and because of the extreme difficulties of retaining the finest-sized particles, some fine coal finds its way into the streams. Erosion from old banks of accumulated fine coal wastes is another source of material which enters the streams.

After the coal is mined and brought to the surface of the ground with associated impurities, it is sent through "breakers" or preparation plants where the coal is separated from the impurities and sized for market. In the early days of the industry all the coal was prepared dry, and only the large pieces were marketed. The fine-sized material was discarded to waste piles. As the output of the industry increased during the nineteenth century, uses were developed for somewhat smaller sizes down to and including pea coal. Early in the twentieth century, sizes smaller than pea were developed and used, but it was not until after World War I that preparation of the so-called steam sizes began commercially. This was largely No. 3 buckwheat which is screened over a $^{3}/_{32}$-inch round-hole screen. At present various sizes down to and including No. 5 buckwheat are prepared from current mining and bank reclaiming operations. No. 4 and No. 5 buckwheat and smaller sizes are generally used for steam production in large boilers.

Since 1907 processing of anthracite has undergone extensive changes as a result of market demands for cleaner coal and the gradual, but progressive, utilization of the finer sizes. Wet washing methods were developed which used water to effect separation