Disposal Of Spent Sulfate Pickling Solutions

An analysis of methods for treating spent solutions resulting from sulfuric acid pickling to reduce stream pollution



Reference Data Publication compiled by

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OHIO RIVER VALLEY WATER SANITATION COMMISSION

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From the Commission's viewpoint...

This manual, prepared under the direction of a voluntary industry committee, is one of a series being sponsored by the Ohio River Valley Water Sanitation Commission for the promotion of pollution control. The subject - disposal of spent pickling solutions - is one that was selected by the Steel Industry Action Committee as of primary significance to the industry and to the Commission.

The manual has a two-fold purpose. For the entire steel industry it is intended to provide a compendium of authoritative information on a complex waste disposal problem, which is a first step in developing corrective measures. For those who must reach decisions with regard to pollution regulation it furnishes important factual data. Thus, the manual supplies basic background for mutual understanding and action.

It is with great satisfaction that the Commission acknowledges this joint contribution of Dr. Richard D. Hoak, fellow of the American Iron and Steel Institute, and a subcommittee of the Steel Industry Action Committee under the chairmanship of Dr. Thomas F. Reed, U. S. Steel Company. Messrs. John E. Kinney and Elmer Rohmiller of the Commission staff edited the manual and executed the layout.

EDWARD J. CLEARY

Executive Director and Chief Engineer A word from the Sub-committee...

This manual on the Disposal of Spent Sulfate Pickling Solutions has been prepared to assist both public health officials and industrial management and technical personnel. It presents a condensation of the voluminous literature on this subject as well as a brief analysis of the applicability of the various methods. A subsequent manual will present a critical evaluation of the more significant disposal processes with some appraisal of their economic potential.

The member companies of the Steel Industry Action Committee of the Ohio River Valley Water Sanitation Commission through their membership in the American Iron and Steel Institute have been among the sponsors of a fellowship on stream pollution established in 1938 at the Mellon Institute of Industrial Research. Acting on the request of the Steel Industry Action Committee to the American Iron and Steel Institute, Dr. R. D. Hoak, Fellow at the Institute, drafted the text of the manual in collaboration with the Sub-committee on Spent Pickling Solutions of the Action Committee. The committee thanks the American Iron and Steel Institute, and Dr. Hoak for their gracious assistance.

The manual is published by the Ohio River Valley Water Sanitation Commission. We thank the Commission and its staff for their invaluable assistance in preparing the manual and in its publication.

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Steel Cleaning Operation Utilizing A Continuous Bath Of Sulfuric Acid

DISPOSAL OF SPENT SULFATE PICKLING SOLUTIONS

The removal of oxide scale from steel prior to further processing is an essential step in the manufacture of many steel products. Such major items as sheets, strip, wire and pipe are descaled by immersion in an acid bath for a short period. This operation is called pickling. Dissolution of part of the scale and some of the base metal results in depletion of the acid and accumulation of iron salts in the bath; for this reason the solution eventually loses its effectiveness and must be discarded.

Spent liquor, in the past, has frequently been discharged into adjacent water bodies, but it is becoming evident that this method of disposal is not always applicable. There is nothing improper in the water carriage of wastes, but the use of streams to carry away excessive amounts of waste may interfere with proper stream usage in the best interests of all. For this reason, domestic sewage and many industrial wastes require treatment to remove or alter their objectionable characteristics before they are discharged.

Necessity for Abatement

The need for and degree of treatment required by spent pickling solution in any given case can be determined only after an appraisal of the characteristics of the waste, the present condition of the stream, and the relative volumes of effluent and stream flow. Proper evaluation of stream conditions as a factor in establishing the required degree of waste purification is a matter that merits the serious attention which regulatory bodies and industry are presently according it through such cooperative efforts as the Industrial Action Committees of the Ohio River Valley Water Sanitation Commission.

Where streams already carry a heavy burden of wastes, especially acid mine water, discharge of a moderate amount of pickle liquor might be completely unobjectionable. On the other hand, the acidity of waste pickle liquor may reduce the pH of some streams to such an extent that the flora and fauna will be altered or destroyed.

It is not the purpose of this Manual to discuss at length the proper stream control measures; quite clearly spent pickle liquor will require treatment in some cases. Accordingly, this Manual will present in summary the characteristics of the waste and available methods for treating it.

Pickling Process

A variety of acids (sulfuric, hydrochloric, nitric, hydrofluoric, phosphoric, individually and in combination) is used to pickle steel, depending on the kind of product being processed; but sulfuric acid accounts for more than 90 percent of the tonnage pickled. This Manual is, therefore, concerned only with methods for handling sulfate liquors.

Steel is pickled in both batch and continuous equipment. In the former, the products are suspended in an acid bath, with or without agitation, until pickling is complete; the time of immersion may vary from ten minutes to an hour or more. The spent liquor usually contains from 0.5 to 2 per cent free acid and 15 to 22 per cent ferrous sulfate, as FeSO4. In continuous pickling, steel strip from a coil passes through a scale-breaker, an automatic welder or stitcher where a fresh coil can be joined to the strip ahead, a series of tanks containing pickling liquor, a rinsing device and a dryer; finally it is recoiled. The time of passage of the strip is such that total pickling time may be less than 30 seconds. The composition of the waste liquor from a continuous pickler will generally fall in the range 5 to 8 per cent free acid and 14 to 16 per cent ferrous sulfate.

Wastes Increase With Output

The tonnage of steel products that require pickling has increased rapidly. The first pickled sheets were made in 1891 when the annual ingot production was 4,372,747 net tons.⁽²⁸⁾ In 1950 there were 96,836,075 net tons of carbon steel manufactured.⁽²⁾ Since about 21% of all steel is pickled at some stage in the production of finished products, the enormous growth of this operation is apparent. An accurate estimate of the volume of spent pickle liquor is difficult to obtain, but it is probably in excess of 600 million gallons annually -- equivalent to 700 tank car trains, each a mile long. The rapid growth of the industry, which is still continuing, has contributed to the difficulty of reaching a universally satisfactory solution to the spent liquor disposal problem.

Good-Housekeeping First

Since appropriate treatment is often necessary to abate stream pollution, it is important to recognize that treatment expense is an actual operating cost, just as are raw materials, power and labor. Accordingly, as in dealing with any other operating cost, the expense is reduced by minimizing the quantity of water, through such process changes as will not seriously effect product quality. Various losses of acid are usually prevented by a periodic process survey. In batch pickling, the liquor should not be discarded until it is indeed spent. This practice not only minimizes the quantity of spent liquor, but reduces the quantity of acid required for pickling. Good housekeeping practices, in general, help reduce concentrated waste to a minimum. Rinse water at the mill should be held to the smallest possible volume where it requires treatment. This can be done by careful control of rinse water usage, more efficient rinsing practice and the use of rinse water to make up fresh baths. Careless use of rinse water may require an excessively large treatment plant.

Collection of spent liquor from several scattered operations to permit treatment in a single plant usually represents a major capital cost. Proper plant location and segregation of strong from weak liquors contribute to reduced capital investment.

Recovery Possibilities

Latent values in waste utilization are sometimes emphasized as incentives to encourage the installation of waste treatment plants. Although many processes have been proposed for recovering useful by-products from pickle liquor, only the manufacture of copperas, $FeSO_4.7H_2O$, has been adopted commercially and then only on a small scale. Successful integration of the by-product recovery process with the steel manufacturing operation is possible in but few selected cases.

The various methods that have been used or proposed for utilizing or disposing of spent pickle liquor are described in the following chapters. Major attention has been given to neutralization techniques because in most instances there is no other alternative. Many by-product recovery processes have been proposed. The more promising of these are discussed in some detail because changing economic conditions may justify their application at some later date.

Disposal Without Treatment

A number of methods have been used, or proposed, for disposing of spent liquors without treatment. These include discharge of the liquor into deep wells, fissures in cavernous limestone, abandoned mines, exhausted oil and gas sands, artificial lagoons, sumps near large bodies of water, and sewers terminating in rivers, lakes and tidewater.

These methods occasionally provide perfectly natural methods for disposing of spent pickle liquor, but sometimes there are serious objections to each. Wells and limestone fissures may eventually refuse to accept more liquor through sealing of permeable strats by deposition of reaction products. Where the discharge reaches the underground fresh water table, pollution often develops. Artificial lagoons, depending on a combination of bottom seepage and solar evaporation, occupy valuable land area, and evaporation does not always exceed rainfall. Gravel or slag sumps adjacent to large bodies of water have been used successfully, but the action of the liquor may gradually seal the permeable area requiring new pits frequently. Where pickle liquor is discharged into streams or large bodies of water, without proper dispersion, gradual oxidation of its iron may color the receiving water brown in localized areas. This makes them esthetically objectionable, even though the actual pollution effect may be relatively small.

DISCHARGE TO MUNICIPAL SEWERS

Where the community has a sewage treatment plant, it is sometimes advantageous to contract with the municipality for the right to discharge the waste liquor to the sanitary sewer system. This procedure has been used in a number of instances to the mutual benefit of both parties. Ferrous sulfate is a good coagulant for sewage and it improves the clarification in the primary settling tanks; in fact, copperas and lime comprise an accepted method for chemical treatment of sewage. On the other hand, the mill can dispose of its liquor at low cost. There are, however, a number of factors that must be considered when this disposal expedient is contemplated.

Neutralization of Free Acid

The free acid in the liquor must be neutralized to prevent corrosion of sewers and sewage-plant equipment. Although domestic sewage is slightly alkaline, its alkalinity is normally inadequate to neutralize more than a small proportion of the free acid in raw pickle liquor. Soda ash, despite its relatively high price, is generally used for this purpose because it is easy to apply, and because it avoids the danger of sludge deposits.

Uniform Discharge

The partly neutralized liquor should be discharged at a uniform rate, preferably proportioned to the sewage flow. Installation of holding tanks at the mill is necessary to provide such a regulated discharge. A steady flow of liquor simplifies the control of sewage treatment and facilitates addition of neutralizing agent at the mill.

Sludge Volume

Disposal of pickle liquor with sewage affects the operation of the sewage works adversely by increasing the bulk of sludge that must be handled. Where sludge-drying beds are taxed to capacity, acceptance of any considerable volume of pickle liquor would require that they be enlarged.

Pickle Liquor Clogs Air Diffusers

Excessive amounts of pickle liquor cannot be treated in a sewage plant employing the activated sludge process because iron in sewage tends to clog the air diffusion plates in aeration tanks.

NEUTRALIZATION - GENERAL CONSIDERATIONS

Treatment of waste pickle liquor with an alkaline material to neutralize the free acid and precipitate the iron is practiced widely in the steel industry, particularly by the small producer who usually has no alternative.

Lime Treatment Is Costly

Complete treatment of pickle liquor with lime is costly because it yields no saleable by-product. The resultant sludge often occupies almost as large a volume as the original liquor plus the lime slurry used in the treatment. But the capital costof aneutralization plant is generally much lower than that for a by-product recovery plant. The slurry from the neutralization plant is generally stored in lagoons, where bottom seepage and solar evaporation gradually reduce the volume of water in the sludge. The over-all cost of lime neutralization will range from \$10 to \$20 per ton of acid charged to the picklers. If space is not available for lagooning the slurry, the cost may be much higher. The expense of neutralization, and the extensiveness of its present and future use, dictate the necessity for operating the process with the greatest economy consistent with a satisfactory degree of treatment. Efficient treatment will result from the application of certain basic principles described in the following chapters.

Details of Tanks

The size and structural details of neutralization tanks will depend to some extent on local factors. They must be acid-proof, and of sufficient size to hold a normal batch of liquor plus the lime slurry required; a safe freeboard (at least three feet, or six feet if wetting agent is used) should be included in the calculation of capacity. Where the daily volume of liquor is large, two or more tanks in parallel will reduce down-time.

One or two combination lime slaking and storage tanks may be used, depending on needs. Lime tanks should have agitators, and should be calibrated to permit drawing off known volumes of milk of lime; a float indicator on a scale graduated in gallons per inch is satisfactory.

Quality of Lime

Lime purchased from a manufacturer will usually be of reasonably constant quality, but where a jobber is the supplier shipments may not always come from the same source. In any case, representative samples should be analyzed at sufficiently frequent intervals to insure that the weight of available alkalinity per unit volume of milk of lime is always known with reasonable accuracy. Analysis of each shipment also guarantees that the lime meets contract specifications.

Slaking Lime

When the analysis is known, a quantity of lime should be slaked to yield a milk of the proper density when diluted in the lime tank. Lime should be slaked in the least amount of water, preferably warm, that will produce a heavy slurry, so that the maximum slaking temperature will be developed; too much or too little water during slaking will reduce the reactivity of the slurry. When slaking is complete (15 to 30 minutes), the slurry should be diluted with five or more pounds of water per pound of lime slaked. The milk of lime is then ready for use, but it should be discharged to the treatment tank through a screen to remove unburned stone and coarse grit.

Neutralizing Pickle Liquor

For the treatment of pickle liquor, an appropriate batch of liquor, preferably hot, is drawn from storage to the neutralization tank. The correct volume of milk of lime is then run into this tank at a moderate rate while the mixture is agitated vigorously. Ample storage for pickle liquor is essential to accommodate fluctuations in mill operations.

Lagooning Sludge

The treated slurry is discharged to a storage lagoon. It usually settles very slowly, and the compacted sludge remains plastic for many years. Design of the lagoon will, therefore, depend principally on the land area available. Generally, it will not be practical to install a weir or other device to draw off the supernatant liquor because most slurries produced conventionally settle too slowly to justify this expense. Where there is no suitable site for a lagoon, the difficulty can sometimes be overcome by constructing a deep sump from which the sludge is removed from time to time by dredging. In other cases it may be necessary to carry the slurry by pipeline or by tank car to a suitable disposal area. Where a pipeline is used, each discharge of slurry should be followed by flushing with clean water to prevent accumulation of sediment in the pipe. Slurry disposal is often quite costly, especially where the mill is located in a built-up metropolitan district.

Definition

Throughout this Manual the mixture in reaction tanks, or being pumped to lagoons, is referred to as "slurry". The material that settles out of the slurry is called "sludge". In slaking lime, the suspension is also called a slurry.

HIGH CALCIUM LIME NEUTRALIZATION

High calcium lime (16), either as quicklime or as the hydrate, is the alkaline agent most commonly used for spent pickle liquor neutralization. This material is highly reactive, and it is usually available in quantity near centers of steel manufacture.

Technique

Screened, slaked quicklime is added to pickle liquor in an acidproof reactor equipped with an efficient agitator. For small installations a slurry of hydrated lime may be preferred; this slurry need not be screened. Proportions of slurry and pickle liquor should be regulated by using the basicity factor-acid value relation (see Appendix I). The reaction proceeds rapidly to completion; after all the lime has been added, mixing should continue for 15 to 30 minutes, depending on the reactivity of the lime.

Slurries produced by the conventional neutralization practice just described cannot usually be efficiently dewatered by filtration or centrifugation. The treated slurry is discharged to a storage lagoon.

Recent pilot plant work(38) has indicated an advantage in adding the spent liquor to the lime slurry, instead of the reverse. Recirculation of the mixture through a centrifugal pump until the reaction was completed produced a slurry that could be satisfactorily dewatered on a rotary vacuum filter. The same investigation disclosed that up to 75% of the filtrate could be substituted for fresh water in slaking the lime. This use of filtrate improved slurryfilterability and resulted in a substantial saving of water.

Reactions

The fundamental reactions that take place when a sulfate liquor is neutralized with lime may be written:

 $\begin{array}{r} H_{2}SO_{4} + Ca(OH)_{2} \longrightarrow CaSO_{4} + 2H_{2}O \\ Fe_{2}(SO_{4})_{3} + 3Ca(OH)_{2} \longrightarrow 3CaSO_{4} + 2Fe(OH)_{3} \\ FeSO_{4} + Ca(OH)_{2} \longrightarrow CaSO_{4} + Fe(OH)_{2} \\ MnSO_{4} + Ca(OH)_{2} \longrightarrow CaSO_{4} + Mn(OH)_{2} \\ 2Fe(OH)_{2} + 1/2 O_{2} + H_{2}O \longrightarrow 2Fe(OH)_{3} \end{array}$

13



HIGH CALCIUM LIME NEUTRALIZATION OF PICKLE LIQUOR Efficiency depends on complete slaking and effective mixing. These reactions occur substantially in the order given. That is, the free acid will react first, followed by the small amount of ferric sulfate that is usually present, then the ferrous sulfate and manganous sulfate (all sulfate liquors contain a few hundredths of one percent of manganese), and, finally, the ferrous hydroxide will oxidize to ferric hydroxide. The extent to which this oxidation occurs will depend on the length of the mixing period and the effectiveness of aeration. In normal practice only a small percentage of the iron will be oxidized.

The actual reactions are undoubtedly more complex than those given above. For example, ferric iron forms basic sulfates whose composition is a function of pH, concentration, temperature and other factors. But quantitative calculations can safely be based on the simplified equations. When acids other than sulfuric are present, the reactions are analogous to those given for sulfates, but it should be noted that calcium chloride and calcium nitrate are very soluble, while calcium fluoride and calcium phosphate are insoluble.

The hydrated iron oxides that precipitate are very insoluble. Calcium sulfate is slightly soluble, about 2 grams dissolving in a liter of water, and it tends to form supersaturated solutions at elevated temperatures. The slurry from the neutralization thus consists of a mixture of hydrated iron oxides and calcium sulfate.

Summary

Local conditions are so variable that only general principles can be outlined for any waste-treatment plant, but conventional neutralization involves no problems of design or operation.

Pickle liquor is generally treated in batches of convenient size. Liquor dumping schedules at the mill are governed by rate of operation and type of steel being pickled. The neutralization plant (Fig. 1) should therefore be provided with adequate pickle liquor storage tanks for averaging its composition, thereby simplifying the neutralization operation. The discharge pipe from the storage tank should be equipped with a screen to prevent refuse from damaging pumps.



DOLOMITIC LIME NEUTRALIZATION OF PICKLE LIQUOR... differs from high calcium lime treatment in that steam is used to raise the temperature and air is used for aeration.

DOLOMITIC LIME TREATMENT

Dolomitic lime is less reactive than high calcium lime, but it has a substantially higher basicity (17). The lower reactivity is due to the slight solubility of magnesium oxide. Reactivity is decreased when dolomitic limestone is calcined, because calcium carbonate decomposes at a higher temperature than magnesium carbonate, and by the time the calcium carbonate is completely calcined the magnesium oxide formed earlier is somewhat overburned. The higher basicity of this compound is due to the lower combining weight of magnesium oxide. Basicity factors for dolomitic quicklimes are about 17% higher than those for high calcium quicklimes, and about 27% higher for the corresponding hydrates.

Technique

Pickle liquor can be neutralized with dolomitic lime in equipment similar to that used for high calcium lime (Fig. 2), and the general observations made on pp. 13-16 apply here. If the full basicity of dolomitic lime is to be utilized, however, several additional steps must be taken.

Using the quantity of dolomitic lime indicated by the basicity factor-acid value relation (Fig. 17), four to six or more hours may be required for complete precipitation of the iron in pickle liquor. Reaction time can be reduced, however, by adding an excess of the agent; very roughly, and within limits, each 5% excess reduces the reaction time about an hour. Reaction time can also be shortened by increasing the temperature; this can be accomplished in practice by treating the pickle liquor before it has had an opportunity to cool appreciably from the pickling temperature (180-200°F). Increasing the rate of oxidation of the precipitated ferrous hydrate increases the reaction rate considerably; this effect can be achieved by introducing diffused air. Experimental work has shown that pickle liquor can be completely treated with dolomitic lime in about an hour if a 5% excess is used, the liquor is treated hot, and aeration is provided.

The magnesium-oxide component of dolomitic lime hydrates much more slowly than its high calcium counterpart. This makes it desirable for slaked dolomitic lime to stand overnight before use.

The difference in reactivity between dolomitic and high calcium limes has been demonstrated by experimental work. Nine types of lime, two high calcium and seven dolomitic, supplied by an Eastern Pennsylvania manufacturer, were investigated. The samples were:





RATE OF REACTION OF VARIOUS LIMES WITH DILUTE PICKLE LIQUOR AT 25°C ... The reaction time with dilute pickle liquor is much longer than with acid alone.

			Sample N	umber				
3	4	5	6	7	8	9	10	11
1.51	2.69	3.15	4.13	1.12	2.72	2.18	1.02	1.55
0.88	0.70	0.70	0.53	0.95	0.48	0.57	0.60	1.02
94.17	55.03	54.95	53.99	71.40	45.04	41.77	42.01	45.90
0.65	40.70	40.10	40.52	0.59	33.02	29.73	29.69	32.75
2.58	0.68	1.05	0.96	25.90	18.93	25.15	26.54	18.67
99.79	99.80	99.95	100.13	99.96	100.19	99.40	99.86	99.89
a								
0.9508	1.1202	1.1109	1.1071	0.7222	0.9126	0.8339	0.8357	0.9275
0.9515	1.0837	1.0855	1.0594	0.7045	0.8611	0.8302	0.8410	0.8876
0.9517	1.1189	1.1351	1.1027	0.7225	0.8952	0.8364	0.8389	0.9115
	3 1.51 0.88 94.17 0.65 <u>2.58</u> 99.79 a 0.9508 0.9515 0.9517	3 4 1.51 2.69 0.88 0.70 94.17 55.03 0.65 40.70 2.58 0.68 99.79 99.80	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Sample Number 3 4 5 6 7 1.51 2.69 3.15 4.13 1.12 0.88 0.70 0.70 0.53 0.95 94.17 55.03 54.95 53.99 71.40 0.65 40.70 40.10 40.52 0.59 2.58 0.68 1.05 0.96 25.90 99.79 99.80 99.95 100.13 99.96 a 0.9508 1.1202 1.1109 1.1071 0.7222 0.9515 1.0837 1.0855 1.0594 0.7045 0.9517 1.1189 1.1351 1.1027 0.7225	Sample Number 3 4 5 6 7 8 1.51 2.69 3.15 4.13 1.12 2.72 0.88 0.70 0.70 0.53 0.95 0.48 94.17 55.03 54.95 53.99 71.40 45.04 0.65 40.70 40.10 40.52 0.59 33.02 2.58 0.68 1.05 0.96 25.90 18.93 99.79 99.80 99.95 100.13 99.96 100.19 .a 0.9508 1.1202 1.1109 1.1071 0.7222 0.9126 0.9515 1.0837 1.0855 1.0594 0.7045 0.8611 0.9517 1.1189 1.1351 1.1027 0.7225 0.8952	Sample Number3456789 1.51 2.69 3.15 4.13 1.12 2.72 2.18 0.88 0.70 0.70 0.53 0.95 0.48 0.57 94.17 55.03 54.95 53.99 71.40 45.04 41.77 0.65 40.70 40.10 40.52 0.59 33.02 29.73 2.58 0.68 1.05 0.96 25.90 18.93 25.15 99.79 99.80 99.95 100.13 99.96 100.19 99.40 0.9508 1.1202 1.1109 1.1071 0.7222 0.9126 0.8339 0.9515 1.0837 1.0855 1.0594 0.7045 0.8611 0.8302 0.9517 1.1189 1.1351 1.1027 0.7225 0.8952 0.8364	Sample Number345678910 1.51 2.69 3.15 4.13 1.12 2.72 2.18 1.02 0.88 0.70 0.70 0.53 0.95 0.48 0.57 0.60 94.17 55.03 54.95 53.99 71.40 45.04 41.77 42.01 0.65 40.70 40.10 40.52 0.59 33.02 29.73 29.69 2.58 0.68 1.05 0.96 25.90 18.93 25.15 26.54 99.79 99.80 99.95 100.13 99.96 100.19 99.40 99.86 a0.9508 1.1202 1.1109 1.1071 0.7222 0.9126 0.8339 0.8357 0.9515 1.0837 1.0855 1.0594 0.7045 0.8611 0.8302 0.8410 0.9517 1.1189 1.1351 1.1027 0.7225 0.8952 0.8364 0.8389

TABLE I. Analyses and Basicity Factors of Nine Limes

^a Basicity factor - gram equivalent CaO/gram sample. HCl factors and H₂SO₄ factor for sample 3 determined by boiling 15 minutes; others, 30 minutes.



Number

Material

3.	High calcium lime
4.	Shaft-kiln dolomitic lime
5.	Rotary-kiln dolomitic lime
6.	60-40 blend of shaft- and rotary-kiln dolomitic lime
7.	High calcium lime hydrated at atmospheric pressure
8.	Dolomitic lime hydrated at atmospheric pressure
9.	Dolomitic lime hydrated at 30 lbs. per sq. in.
10.	Dolomitic lime hydrated at 30 lbs. per sq. in. and air-floated
11.	Dolomitic lime hydrated at atmospheric pressure and air-floated

Most of the experimental work was done on Samples 4, 5, 10, and 11, because they represent the usual types of dolomitic limes generally available. The samples were analyzed, and basicity factors were calculated from the analyses and determined experimentally with sulfuric and hydrochloric acids. Resulting data are given in Table I.

Although the experimental data to be reported apply equally well to all dolomitic limes, Eastern Pennsylvania dolomites are less pure than those from other regions. A dolomitic quicklime from Ohio, for example, may contain about 0.8% silica and 0.2% R₂O₃ (iron and aluminum oxides), this lime would contain a slightly higher proportion of calcium and magnesium oxides. The difference will be reflected in the corresponding hydrates, depending upon the extent to which air separation removes impurities.

Determination of basicities by calculation from chemical analyses may be misleading because analyses do not reveal the manner in which the silica and R_2O_3 are combined in the product. The availability of the calcium and magnesium oxides is reduced in proportion to the degree to which these impurities have fluxed during calcination. Other minor factors, such as slaking quality and distribution of impurities between the calcium oxide and magnesium oxide components, cause some uncertainties where basicity factors are calculated.

The rate of precipitation of ferrous iron is a function of the rate at which hydroxyl ions can be supplied at a pH of about 8.5. In illustration of the rate at which dolomitic limes react with an acid solution, compared with high calcium lime, a 0.1 N solution of sulfuric acid was treated with a 2% excess of several limes at room temperature. The results (Fig. 3) show clearly the differences in reaction rates. Similarly, a dilute pickle liquor (10.96 grams ferrous ion and 35.68 grams sulfate ion per liter) was treated with slurries of the same agents (Fig. 4). When dilute sulfuric acid was neutralized with the limes the reaction with high calcium lime was almost instantaneous, whereas the dolomitic limes reacted slowly, yielding pH values of 8.5 to 9.5 in about 15 minutes. The reaction rates with dilute pickle liquor were much lower; the dolomitic limes could not develop a pH value much above 8, whereas the pH of the high calcium lime mixture was 9.3 and still rising when the test was concluded. For complete precipitation of ferrous iron a pH of about 9.3 is required.



RATE OF IRON PRECIPITATION FROM PICKLE LIQUOR BY DOLOMITIC LIME ... Increased temperature, excess lime and rapid agitation all increase the rate.

The rate of precipitation of iron by these agents was traced by treating a pickle liquor (56 grams ferrous ion, 180 grams sulfate ion per liter) at room temperature with a 5% excess of the lime slurries. The slurries were stirred constantly with electric mixers. Samples were withdrawn at intervals and filtered, and the filtrates were analyzed for iron. The data are shown graphically in Fig. 5.

The effects of temperature, excess lime, and aeration by rapid agitation were studied separately. Each of these factors was effective in reducing the reaction time between pickle liquor and dolomitic lime. The results attained when pickle liquor was treated at 80° C. with a 5% excess of dolomitic lime and aerated by rapid agitation are shown in Fig. 6. Comparison of this graph with Fig. 5 will illustrate the improvement in reaction rate.

Reactions

The basic reactions that occur when pickle liquor is neutralized with dolomitic lime may be written:

 $2H_{2}SO_{4} + Ca(OH)_{2} + Mg(OH)_{2} \longrightarrow CaSO_{4} + MgSO_{4} + 4H_{2}O$ $2Fe_{2}(SO_{4})_{3} + 3Ca(OH)_{2} + 3Mg(OH)_{2} \longrightarrow 3CaSO_{4} + 3MgSO_{4} + 4Fe(OH)_{3}$ $2FeSO_{4} + Ca(OH)_{2} + Mg(OH)_{2} \longrightarrow CaSO_{4} + MgSO_{4} + 2Fe(OH)_{2}$ $2MnSO_{4} + Ca(OH)_{2} + Mg(OH)_{2} \longrightarrow CaSO_{4} + MgSO_{4} + 2Mn(OH)_{2}$ $2Fe(OH)_{2} + 1/2 O_{2} + H_{2}O \longrightarrow 2Fe(OH)_{3}$

These equations have been written for a true dolomitic lime (lime and magnesia in equimolar proportions), and on the assumption that all the magnesia has been hydrated by slaking. But the lime and magnesia content of many magnesian limes is not equimolar, and slaking may not completely hydrate the magnesia. These equations must therefore be considered only as representative of reactions that may occur. As in high calcium lime treatment, the reactions may be quite complex, but the basicity factor-acid value relation provides a simple method for determining the amount of slurry that will be required by any pickle liquor.

Summary

With the exceptions noted under Technique, the treatment of pickle liquor with dolomitic lime is the same as for high calcium lime. Dolomitic lime produces a bulkier sludge than high calcium. The sludge has a lower dry solids content, but it settles much more slowly. The basicity advantage of dolomitic lime over high calcium places the two agents on a relatively equivalent basis for pickle liquor treatment. Where large volumes of liquor must be treated, the saving in cost of alkaline agent will permit the use of several expedients to reduce the reaction time without exceeding the cost for high calcium lime.





SCHEMATIC ARRANGEMENT OF LABORATORY APPARATUS USED FOR NEUTRALIZATION-OXIDATION STUDY OF PICKLE LIQUOR.

NEUTRALIZATION WITH AIR OXIDATION

The high cost of handling the large volume of sludge produced where pickle liquor is treated with lime by conventional methods directed research attention to the development of a process for reducing its volume or increasing its filterability. Both of these objectives were attained in the laboratory in the neutralization oxidation process. (19)

Technique

Controlled oxidation to ferroso-ferric oxide of the ferrous hydrate that precipitates when pickle liquor is treated with an alkaline material, is the fundamental principle on which the process operates. Basically, the process consists of feeding pickle liquor at a predetermined constant rate to an alkaline bath in a reactor (Fig. 7), where the temperature is maintained above 75°C. and efficient aeration is provided. The vertical baffle shown in the sketch creates the necessary turbulence.

The basic principles of the process were established by using a cyclic continuous method of operation, whereby pickle liquor was fed at a constant rate to a volume of slurry from a previous run, equal to about half the capacity of the reactor. Before the pickle liquor feed was started, the alkaline agent, equivalent to the volume of liquor to be added, was mixed with the slurry in the reactor. At the conclusion of a run the reactor was drained to its mid-point and a new cycle started immediately. This method was used because equipment was not available during development of the process for feeding alkaline agent at a uniform rate, but supplemental runs, where the alkaline material was added manually, showed that, with proper feeding devices, the process could be operated continuously without difficulty.

Successful operation of the process depends primarily on balancing the rate of precipitation of iron with the rate of oxidation of ferrous hydrate. These rates must be so controlled that the iron in the precipitate will have a ferric-ferrous ratio between 2 and 5, preferably between 2.5 and 3.5, while the temperature of the bath is maintained high enough to promote the formation of ferroso-ferric oxide. If the reactor provides efficient dispersion of air, the only variables to be considered are the rates of feed of pickle liquor and air, and the optimum excess of alkaline agent. These can readily be established by a few trial runs.

The process development work was based on two strengths of pickle liquor. One contained 60 grams ferrous ion and 200 grams sulfate ion per liter, representing the liquor discharged by continuous strip picklers. The other was exactly half that strength, to illustrate conditions to be expected where the strong liquor is diluted with rinse water. Results of typical runs for magnesia, high calcium lime, and dolomitic lime with half- and fullstrength pickle liquor are given in Table II.

Run*	%	Amount Agent, Stoich.	S.P.L. Rate ml./min.	Slurry pH	<u>Fe+++</u> Fe++	Fe in Sup't g./l.	Initial Settling, in./min.	Final Sludge Volume, % Original
MgO -	half	105	270	6.9	3.36	0.03	0.85	8
MgO -	full	104.5	117	7.4	2.69	0.04	0.53	16
HiC -	half	105	285	9.0	2.53	0.00	0.58	35
HiC -	full	105	140	9.5	2.50	0.00	0.40	58
Dol -	half	110	108	8.0	3.50	0.01	0.78	20.5
Dol -	full	110	75	6.9	2.53	0.02	0.60	30

TABLE II. EFFECT OF NEUTRALIZATION-OXIDATION PROCESS AT 80°C IN REDUCING SLUDGE VOLUME

* Represents magnesia, high calcium lime, and dolomitic lime, with halfand full-strength liquor.

Supernatant liquors from magnesia and dolomitic lime treatment contained small amounts of soluble iron. (Table II). This can be eliminated by continuing the air supply for a short time after the pickle liquor feed has been stopped.

The co-precipitated calcium sulfate accounts for the major portion of the sludge bulk. This may be seen by comparing the final sludge volumes for magnesia with those for the other two agents. The sludge volume produced by full-strength liquor with high calcium lime was only 65% greater than that from half-strength liquor; for dolomitic lime the figure was 50%. This shows the advantage of treating strong liquor by this process.

Only the initial settling rates are shown in Table II. In all cases, sedimentation was complete in less than an hour, and in most runs in less than 15 minutes.

Filtration tests on the slurry resulting from high-calcium lime neutralization by this process, using a standard filter disk with an effective area of 0.1 sq. ft., showed a rate of 68 gallons of filtrate and 400 pounds of wet cake per square foot per hour. The wet cake averaged about 60% dry solids. This filtration rate is about 20 times that of the slurry from conventional high calcium lime treatment. The filtration rate of dolomitic lime slurry was about one-third that of the high calcium rate. Filtration studies were not made on the magnesia slurry because its small volume would lend itself to separation in a sludge thickener.

Reactions

The only important reactions in this process are those involving the precipitation of iron, its rate of oxidation, and its conversion to ferroso-ferric oxide. Sulfates, whose identity will depend on the kind of alkaline agent used, will be by-products, just as they are in conventional neutralization practice.

Ferrous hydroxide, $Fe(OH)_2$, and ferric hydroxide, $Fe(OH)_3$, are definite compounds. They occur, however, only under carefully controlled conditions, and it is preferable to speak of hydrated ferrous and ferric oxides, indicating an indefinite degree of hydration, because these are the compounds that precipitate when pickle liquor is neutralized. For this reason, hydration is shown as XH₂O in the equations, but X does not necessarily always have the same value. X-Ray diffraction analysis of the magnetic iron oxide formed in this process indicates that the compound is primarily magnetite, Fe_3O_4 , and that it has a particle size of about 0.1 micron.

Summary

This process offers a new approach to pickle liquor neutralization. It converts the precipitate in the slurry into a mixture that settles and filters rapidly, yielding the smallest possible sludge volume. This feature has special value for companies with a limited lagoon area.

Proper control of the ferric-ferrous ratio might appear to pose a difficult operating problem. This is not the case, because the value of the ratio is not critical. Although it can be determined analytically in a few minutes, the process can easily be controlled by observing the settling rate of the sludge-slurry interface and testing the supernatant for the presence of soluble iron.

LIMESTONE AS A NEUTRALIZING AGENT

Lime treatment of spent pickle liquor has been common for many years, but the development of processes using limestone for this purpose has received scant attention.(16) Limestone would appear to be a logical alkaline agent for pickle liquor treatment because of its wide geographical distribution and relatively low price. It has been used occasionally by permitting the liquor to percolate through beds of lump stone, but the results have usually been unsatisfactory. When sulfate pickle liquor reacts with lump limestone, the deposit of a relatively impervious layer of calcium sulfate prevents the utilization of more than a small fraction of its alkalinity. The upflow limestone process developed by Gehm(11) for neutralizing acidic wastes is applicable to dilute pickle liquors and rinse water, but it is unlikely to be satisfactory for strong liquor because of clogging by the ferrous hydrate precipitate.

Pulverized limestone can be utilized much more effectively than lump or crushed stone because the fine particles tend to react more completely. Such material will quickly neutralize free acid and precipitate ferric iron in pickle liquor, but it will not precipitate ferrous iron completely, even if reduced to extreme fineness, because limestone cannot produce a pH as high as the required 9.3. But the rate of oxidation of ferrous iron increases rapidly with increasing pH, and, where oxygen can be supplied by aeration, many pulverized limestones will precipitate ferrous sulfate completely if the oxidation of the iron is allowed to go to substantial completion.

Technique

Treatment of pickle liquor with pulverized limestone is simpler than treatment with slaked lime because the limestone can be added dry. But a much longer reaction time is required even if oxidation is accelerated by diffused air or a turbo-type mixer-aerator. The quantity of pulverized stone determined from the basicity factor-acid value relation (Appendix I) is added to the pickle liquor in an acid-proof tank. The mixture is agitated and aerated until a test shows that all the iron has been precipitated. Foaming is kept to a minimum at one plant by adding all the limestone at once to just enough pickle liquor to form a heavy slurry. The balance of the liquor is then added gradually. Adequate ventilation must be provided where this treatment is used in a closed building.

Where a cheap source of reactive high-calcium pulverized limestone is available, use of this material instead of lime may result in an over-all economy. In comparing the cost of raw materials, note that about 1.9 times as much limestone as high calcium quicklime, or 2.3 times as much as dolomitic quicklime, will be required for neutralization. Pulverized limestones vary widely in their rate of reaction with pickle liquor. Reaction rates are governed by chemical analysis, fineness, and a specific reactivity, peculiar to each stone, that cannot be evaluated easily except by trial. The amount of magnesium carbonate in a limestone exerts a profound effect on its rate of reaction. Although many other factors affect its reactivity, the rate of reaction appears to be nearly inversely proportional to the quantity of magnesium carbonate it contains (above about 2%). There is a critical particle size which varies with different limestones, but for most purposes the so-called mine-dusting grade, of which 80-85% will pass 200 mesh, is satisfactory.

The screen analysis and the chemical analysis of a number of representative limestones are given in Tables III and IV. The rates of reaction of these stones with a strong pickle liquor (63.8 grams ferrous ion, 209.3 grams sulfate ion per liter) are shown graphically in Fig. 8. Aeration was not used in these runs, except for that resulting from the action of the stirrer.

Limestone	+65	-65 +100	-100 +200	-200 +325	-325
А	0.0%	1.5%	10.0%	28.0%	60.4%
В	2.1	5.9	20.4	37.9	31.2
С	0.0	0.4	0.8	85.0	13.0
D	1.2	3.8	10.3	41.9	40.7
E	0.2	0.7	1.9	15.0	81.7
F	0.2	1.0	12.8	33.6	51.7
G	0.2	1.6	11.7	83.5	2.5
H	0.0	0.3	7.0	33.5	58.0
I	0.0	0.0	4.0	21.5	74.2

TABLE III. SCREEN ANALYSIS OF PULVERIZED LIMESTONES



Limestone	Loss at 150 ⁰ C., %	Acid insol., %	^R 2 ⁰ 3	CaCO3	MgCO3	Basicity Fac- tor,g. CaO/g.
A	0.17	0.73	1.09	93.90	2.26	0.554
В	0.11	0.35	0.49	54.28	44.31	0.600
C	0.00	4.20	0.49	95.33	0.75	0.537
D	0.10	5.60	1.31	87.35	1.05	0.498
E	0.06	0.94	0.29	96.97	0.79	0.554
F	0.13	1.64	0.38	86.97	10.89	0.561
G	0.10	2.21	0.50	96.91	1.17	0.547
Н	0.08	2.35	0.44	95.10	1.50	0.547
I	0.08	3.72	0.68	51.84	42.62	0.576

TABLE IV. ANALYSIS OF PULVERIZED LIMESTONES

The effect of magnesium carbonate when it exceeds about 2% in a limestone is shown in Fig. 8. The curve for U.S.P. magnesium carbonate indicates that it is the physical combination of the magnesium carbonate in limestone that affects its reactivity. The dashed line of Curve B indicates the addition of a 100% excess of limestone. These data show that the low reactivity of most magnesian limestones make them useless for pickle liguor treatment. A dolomitic limestone has recently been found in Tennessee (23) that is superior to some high calcium stones in reaction with sulfuric acid; this has been ascribed to an uncommon crystal structure.

Reactions

Equations for the reactions that take place between pickle liquor and high calcium limestone are:

 $\begin{array}{rl} H_2SO_4 + CaCO_3 \longrightarrow CaSO_4 + H_2O + CO_2 \\ FeSO_4 + CaCO_3 + H_2O \longrightarrow CaSO_4 + Fe(OH)_2 + CO_2 \\ 2Fe(OH)_2 + 1/2 O_2 + H_2O \longrightarrow 2Fe(OH)_3 \end{array}$

Equations for magnesium carbonate are not given because this compound usually reacts too slowly to exert an appreciable effect on the neutralization. The reactions are analogous to those for calcium carbonate.

Oxidation of the precipitated ferrous hydrate provides the driving force that promotes complete precipitation of all the ferrous iron by a substance that, in itself, cannot raise the pH high enough to accomplish this. The tendency of ferrous sulfate to hydrolyze, by the reversible reaction, is the first step in the process. The tendency of the reaction to proceed to

$$FeSO_4 + 2H_2O \implies Fe(OH)_2 + H_2SO_4$$

the right increases with increasing pH; if the pH falls, the products on the left are formed. If no other reactions were allowed to occur, such a system would soon come to equilibrium, i.e., the reaction could go equally well in either direction. But if one or both the products on the right of the equation were removed from the system, the equilibrium would be destroyed and the reaction would continue to go to the right until all the ferrous iron was precipitated. This occurs in limestone neutralization because the acid reacts with calcium carbonate to form calcium sulfate, water and carbon dioxide, and the ferrous hydrate is oxidized to ferric hydrate, thus permitting more ferrous sulfate to hydrolyze. In an actual neutralization all these reactions occur more or less simultaneously, provided sufficient reactive limestone is present. Iron can be completely precipitated experimentally from an efficiently aerated mixture of pickle liquor and pulverized limestone in about one-third the time that is required without aeration.

Summary

In locations where pulverized high-calcium limestone can be purchased at a substantially lower price than the equivalent amount of lime, it can provide an economical agent for pickle liquor neutralization. The simplicity of the operation, the elimination of lime slaking equipment, purchase in bulk to save bagging charges, lack of need for air-tight storage bins, and the fact that a smaller sludge volume is produced than in lime neutralization are factors that should be considered in evaluating the process.

MISCELLANEOUS NEUTRALIZATION AGENTS AND PROCESSES

Four neutralization techniques worthy of mention are: treatment with limestone and lime, dry lime neutralization, neutralization with blast furnace slag, and disposal on molten slag.

Treatment with Limestone and Lime

Pulverized limestone alone often will require more time than can be allowed for complete treatment of pickle liquor, but a combination of this material with quicklime will sometimes permit an economy in operating costs. This method of treatment (16) involves merely the addition of enough high calcium pulverized limestone to neutralize the free acid and precipitate the ferric iron, followed by lime slurry to complete the treatment.

The process is being operated in one steel mill as follows: The proper amount of pulverized limestone is added all at once from a weigh hopper to a batch of pickle liquor. The mixture is stirred until it turns light yellow, indicating that the ferric iron has been precipitated, and mixing is continued about ten minutes longer to expel the liberated carbon dioxide. Most pickle liquor contains enough ferric iron to produce this end point. Milk of lime is then run in until a red color is obtained with phenolphthalein indicator, and the treatment is completed by mixing for a few minutes longer. Phenolphthalein first gives a pink color with an alkali at a pH of about 8.3. From the time the test is taken until the lime feed is turned off, enough lime will normally have been added to raise the pH above 9; at this point complete precipitation of ferrous iron is insured.

Economy of operation can be effected by this process where the spent pickle contains a relatively high concentration of free acid, and where pulverized limestone is cheap compared with quicklime. In some localities pulverized limestone costs as much as quicklime on a basicity basis, and in that case the split treatment process would show no advantage. But the material can frequently be bought very cheaply, especially from quarries that do not operate lime plants.

A similar procedure might be employed where it was desired merely to reduce the time required for complete treatment with pulverized limestone. A reactive limestone will precipitate about 70% of the iron in an hour (Fig. 8), but as much as three hours more may be required to remove the remainder. If, at the end of an hour, enough high calcium lime slurry were added to raise the pH of the slurry to about 9.3, the reaction would be complete in a few minutes. Such practice might result in worthwhile economies.

Dry Lime Neutralization

A neutralization procedure which uses dry lime ⁽²⁵⁾ has been developed for shops producing no more than several thousand gallons of spent pickle liquor per day. A 100 to 300% excess of dry pulverized quicklime or hydrate is fed to the pickle liquor in a reactor equipped with an agitator. As the liquor is neutralized, the excess lime forms a granular sludge that can be readily dewatered on a vacuum filter or in a basket centrifuge. Although this great excess of lime could not be justified for a large mill, the process may appeal to small plants because of its simplicity and the fact that the sludge need not be lagooned.

Neutralization with Blast Furnace Slag

A method for using blast furnace slag to treat pickle liquor calls for pouring molten slag into such a volume of liquor that most of the water is vaporized, leaving a granular mass containing 10-12% moisture⁽¹²⁾. This material could be used advantageously as a filler for fertilizer because of its content of trace elements. Practical development of this process would lower the cost of pickle liquor treatment in some areas.

Disposal on Molten Slag

A very simple pickle liquor disposal method that causes no complaints has been adopted by one steel company. When molten blast furnace slag is hauled to the dump, one or more tank cars of spent liquor are attached to the end of the train. After the slag ladles have been emptied, the train is pulled ahead and the liquor discharged on the slag. Less than an hour is required to vaporize 20,000 gallons of pickle liquor completely. Succeeding taps of slag are deposited at the same place, and any iron salt that might have escaped decomposition is covered with molten slag. It might be supposed that aerial pollution would result from this procedure, but this is not the case. If one stands directly in the dense vapor, a slight prickling sensation in the nose is the only noticeable effect; at a distance of ten feet there is only a faint, unobjectionable odor.
FACTORS GOVERNING SELECTION OF NEUTRALIZATION PROCEDURE

Pickle-liquor neutralization plants must be properly adapted to local conditions, and to the alkaline agents available.

Two types of factor affect the choice of agent: (a) those fixed by the agent itself, such as basicity factor (See Appendix I), delivered price (18), reactivity, etc.; and (b) those set by the conditions prevailing at a given mill, such as operating schedule, area available for the treatment plant, characteristic of the receiving stream or sewer system, and the like. Generally, the last-mentioned group of factors will be relatively unalterable, and an agent must be selected to meet these requirements.

Space Available

Where little or no land is available for lagooning the sludge from the treatment plant, the agent that yields the most settleable (or dewaterable) sludge must be used, even though its cost be comparatively high. Sludge handling may cost several times as much as the actual neutralization, and any agent that will substantially reduce sludge volume will permit the payment of a correspondingly higher price for it.

Reaction Time

The reaction rates of available alkaline agents may cover a considerable range. Where reaction time is limited by the space assigned to the neutralization plant, the most reactive agents are indicated. Where the dumping schedule of the pickling plant allows relatively long periods of time to elapse between batches, one of the less reactive, but cheaper agents, such as pulverized high-calcium limestone, may be used to advantage.

A condensed summary of the reactivities of certain common agents is given in Table V. Reactivities were compared under four reaction conditions: (1) room temperature, no aeration; (2) 60° C., no aeration; (3) room temperature, with aeration; and (4) 60° C., with aeration.

Pickle Liquor Volume

At plants where a large volume of liquor is produced, and there is adequate space for the necessary treatment facilities, it may be possible to reduce operating costs by designing a plant of sufficient size to utilize one of the less reactive agents. For example, pickle liquor can be given complete treatment (precipitation of all the iron) with pulverized high-calcium limestone in a plant providing efficient agitation and aeration; several hours' reaction time is required by this agent as compared with 15 to 20 minutes for lime slurry, but its cost may be a third less, on a basicity factor basis. Operating economies can sometimes be realized by using continuous operation instead of the conventional batch method.

TABLE V. REACTIVITY OF ALKALINE AGENTS WITH PICKLE LIQUOR

(Iron unprecipitated after 6 hours, grams per liter)

	No Ae:	ration	_ With Aer	ation
Agent	Room Temp.	60°C.	Room Temp.	60°C.
NaOH	a	a	a	a
Na ₂ CO ₃	0 in 0.75 hr.	0 in 0.75 hr.	0 in 0.75 hr.	0 in 0.5 hr.
MgO (reactive)	0 in 3 hr.	0.72	0 in 0.5 hr.	0 in 0.25 hr.
MgO (unreactive)	14.08	14.08	11.99	2.50
CaO	0 in 0.25 hr.	0 in 0.25 hr.	0 in 5 min.	0 in 5 min.
Ca0.Mg0	1.88	3.14	1.04	0.30
Ca(OH)2	0 in 0.5 hr.			
Ca(OH)2.MgO	1.23	1.53	0.55	0 in 3.5 hr.
Acetylene sludge Ca(OH) ₂	1.66	1.04	0 in 3.5 hr.	0 in 3.5 hr.
Cement dust (reactive)	9.44	8.02	2.43	0 in 4 hr.
Cement dust (unreactive)	13.81	14.00	8.02	3.49
CaCO3, precipitated	8.95	5.17	0 in 2 hr.	0 in 1.5 hr.
CaCO3, limestone	20.40	18.80	2.95	0.03

^a Reaction practically instantaneous.

Water Supply

Some mills have a limited supply of process water, and, in consequence, must practice water conservation. Where it is desirable to re-use the clarified effluent from a pickle liquor treatment plant, the alkaline agent used should produce the lowest concentration of dissolved salts, e.g., high-calcium lime. Clarified effluent can be used for preparing fresh pickling batches, for lime slaking, or for low temperature cooling.

Availability of Agent

If a plant is designed to use a particular agent, it is obvious that the designer should be certain of its long-term availability. This caution applies especially to situations where the most desirable alkaline agent is a waste product of another industry.

Cost Comparison of Alkaline Agents

It is axiomatic that the cheapest agent capable of fulfilling the requirements should be used. Delivered cost per ton is not usually a sound criterion of actual cost, and wherever possible even cheap agents should be held to specifications by routine analysis of each shipment.

Selection of the proper alkaline agent should be based on four criteria; cost per ton of available basicity, reactivity, character of sludge produced, and possible by-product recovery. Pickle liquor cannot ordinarily be processed profitably to recover usable by-products. This results principally from the fact that the spent liquor is a relatively dilute solution of low-cost chemicals. In certain localities, however, it may be possible to recover compounds that will pay a substantial part of the cost of operation. For example, if reactive magnesia were to be used as a neutralizing agent, pure magnesium sulphate could be recovered, as well as an iron oxide suitable for pigment manufacture or for conversion to sinter for blast furnace charging. Enterprises of this character should not be undertaken without making a survey of conditions in local chemical markets, or without the assurance that other producers would not flood the market with a competitive compound. The weight given to each of these four factors will depend on local conditions.

When a neutralizing agent is purchased, it is important that the cost be computed in terms of available basicity. Unavailable basicity is worse than useless; not only does it cost as much per ton as the active ingredient, but it increases the volume of sludge that must be handled. Typical basicity factors of a number of agents that have been used to neutralize pickle liquor are listed in Table VI. Division of the delivered price of a material by its basicity factor will yield the cost of a unit of basicity. Actual prices of agents have not been given because they vary between different areas.

It is essential to note that the factors in Table VI are those theoretically attainable under optimum conditions. For example, dolomitic limes have higher theoretical basicities than high calcium limes, but certain precautions must be taken in the neutralization process to realize this advantage, as outlined on pp. 13-16. Basicities of the agents actually available, must be determined under conditions that approximate those in the neutralization plant if they are to serve their purpose properly.

Agent	Grade	Container	Basicity Factor	
Sodium Hydroxide	Flake, 76%	Drums	0.687	
Sodium Carbonate	Dense, 58%	Bags	0.507	
Ammonia	Aqua, 35%	Drums	1.647	
Ammonia	Anhydrous	Tank Car	1.647	
Magnesium Oxide	Powder	Bags	1.306	
High Calcium Hydrate	Chemical	Bags	0.710	
Dolomitic Hydrate	Chemical	Bags	0.912	
High Calcium Quicklime	Pulverized	Bags Bulk	0.941 0.941	
Dolomitic Quicklime	Ground	Bags Bulk	1.110 1.110	
High Calcium Limestone	Pulverized	Bags Bulk	0.489 0.489	
Dolomitic Limestone	Pulverized	Bags Bulk	0.564	

TABLE VI TYPICAL BASICITY OF VARIOUS ALKALINE AGENTS

Several alkaline materials that are quite costly as compared with high calcium lime are listed in Table VI. Sodium hydroxide would not be used for pickle liquor treatment unless recovery of iron oxide and sodium sulfate were contemplated; such a process would not usually be economically sound, but where there is a local market for sodium sulfate it might reduce the

TABLE VII. INITIAL SLUDGE SETTLING RATES AND FINAL SLUDGE VOLUMES^(a) FOR VARIOUS ALKALINE AGENTS

		No Aera Roor Tempera	ation n ature	60°c		With Aer Room	ration n ature	60°c		
	Alkaline	Initial Settling Rate in % of Original Volume	Final Volume As % Of Origi- nal							
	Agent	Per min.	Volume							
>	NaOH	0.03	83	0.04	79	0.03	84	0.00	26	
\geq	Na2 CO3	4.4	16	3.6	22	5.6	14	2.4	20	
	MgO (reactive)	0.22	58	0.55	44	0.18	44	0.00	100	
	MgO (unreactive)	Ъ	Ъ	Ъ	ъ	Ъ	Ъ	Ъ	b	
	CaO	0.01	91	0.07	69	0.01	92	0.01	81	
	CaO.MgO	0.00	100	0.10	70	0.05	51	0.05	57	
	Ca(OH)2	0.07	68	0.13	70	0.01	93	0.03	95	
÷	Ca(OH)2.MgO	0.03	71	0.10	57	0.67	48	0.00	60	
	Acetylene sludge	0.13	75	0.27	69	0.67	70	0.27	80	
	Cement dust (reactive)	1.73	62	1.33	58	1.26	70	1.24	67	
	Cement dust (unreactive)	Ъ	Ъ	Ъ	Ъ	Ъ	Ъ	Ъ	Ъ	
	CaCO3, pptd.	0.67	63	0.63	65	0.13	72	0.2	57	
7	CaCO3, limestone	Ъ	Ъ	Ъ	Ъ	0.57 🖉	46	0.13	77	

^a Final sludge volume attained in 17 to 20 hours.

^b Settling rate meaningless because of small fraction of iron precipitated.

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over-all treatment cost. Sodium carbonate has been used where only the neutralization of free acid is required; it is useful for this purpose because it can be added dry, but, aside from its high price, it is an unsatisfactory agent for complete treatment because of its tendency to form soluble ferrous bicarbonate. A special procedure is necessary where ammonia can be used, and this is described later in the Manual; it would not normally be considered for neutralization on a small scale. Magnesium oxide is a rather costly compound that can be used where it is desired to recover iron oxide and magnesium sulfate; except under unusual circumstances a process of this kind could be used only to reduce the net cost of treatment somewhat. When a pickle liquor neutralization plant is planned, neighboring industries should be surveyed to discover whether a suitable alkaline waste product is available. It happens occasionally that the wastes of two or more industries can be combined to effect a mutually advantageous solution for waste disposal.

Sludge Settleability

The settling character of the sludges from Table V is presented in Table VII. The initial settling rate, in per cent of total volume appearing as supernatant per minute in a 100-ml. cylinder, and a figure for the final sludge volume as a percentage of the original slurry volume are given in parallel columns for each agent under the four reaction conditions. In some cases the sludge compacted to its final volume in several hours, in others a number of days were required. Certain of the agents were so unreactive that only a relatively small proportion of the iron was precipitated; in these cases the settling data were not recorded.

Summary

This chapter has indicated the various economic factors that should be considered in designing a pickle liquor neutralization plant. It has emphasized the fact that care in selecting the most appropriate alkaline agent for a given set of conditions can materially reduce the cost of this method of disposal.

The preceding chapters have reported the most modern neutralization techniques, but it would not be possible to describe every conceivable method that might be employed. Advances continue to be made in this field, and it is to be hoped that the approach to the problem that has been presented will encourage others to seek improved methods. In facing this waste disposal problem it is important to recognize that reduction of waste water volumes to an irreducible minimum is the best kind of economy; pickle liquor treatment processes are always costly.

RECOVERY OF BY-PRODUCTS

Research looking toward useful products from waste pickle liquor has resulted in eighty-odd processes. Few of these have ever been operated on a successful commercial scale.

Copperas not the General Answer

Even the simplest of them -- the recovery of copperas -- has usually been unsuccessful. Actually, the entire market demand for copperas can be satisfied by less than 5% of the pickle liquor output of the steel industry. The production of such a primary by-product cannot be a general answer unless very large new uses for copperas -- which are not in sight -should be discovered and developed.

Restricted Market for Other Products

The same situation holds for any other single product derivable from pickle liquor; the products are all cheap inorganic sulfates and iron compounds. Indeed the only products for which there is any likelihood of use in quantities of the magnitude which here concern us are sulfuric acid, ammonium sulfate, or sodium sulfate with fairly pure iron oxide as a secondary by-product.

Shipping Problems

The combination of a dilute solution and relatively low-cost products prevents the use of any disposal method requiring transportation of raw or finished materials for any great distance. For example, pickling installations and coke plants are generally not contiguous; this is the usual difficulty when trying to combine pickle liquor and coke oven ammonia to produce ammonium sulfate.

Possibility for Research Answer

The possibility that pickle liquor processes will be developed that can break even, or even show a profit, must not be discounted. Research is going forward in many places, but the extensive investigations already made by the steel industry suggest that a periodic review of previously developed processes be made. Economic factors have a disconcerting facility for change.

Available Processes

The various processes that have been proposed fall into a number of classes: Recovery or manufacture of, -

- a. copperas and lower hydrates of ferrous sulfate
- b. copperas and free sulfuric acid
- c. ferrous sulfate monohydrate and sulfuric acid
- d. iron oxide and sulfuric acid
- e. ferric sulfate and sulfuric acid
- f. iron oxide and ammonium sulfate
- g. construction material
- h. manganese concentrate
- i. magnesia
 - j. miscellaneous processes.

These processes have been described in considerable detail, with an extensive bibliography (20). Only the more important processes are outlined here.

RECOVERY OF COPPERAS

Copperas is the only hydrate of ferrous sulfate currently being recovered from spent pickling solution. Recovery of copperas, FeSO₄.7H₂O, from waste pickle liquor is a simple operation (1.7). In batch pickling it is customary to add fresh acid to the bath from time to time to maintain a satisfactory pickling rate. As pickling proceeds, the concentration of ferrous sulfate in the bath gradually increases until it reaches a point at which it inhibits pickling; the spent liquor must then be discarded. The amount of free acid in such a liquor is often too small to justify the expense of recovery. Where copperas recovery is practiced, the waste liquor is run to a tank and heated with enough scrap iron to neutralize the residual acid. The resulting solution is settled to remove suspended matter, and the copperas is recovered as crystals, following either evaporation or refrigeration. These operations must be carried out in acid-proof equipment. A typical flowsheet of copperas recovery is shown in Figure 9, but various modifications of this procedure have been used.

Drying to a Lower Hydrate

Copperas can be dried in a rotary kiln to yield lower hydrates such as siderotilate, FeSO4.5H2O, but the drying must be carefully controlled because copperas, if heated too rapidly will melt in its water of crystallization and cause operating difficulties. Copperas is dried beyond the trihydrate by this method. Where ferrous sulfate with a low water content is desired, it is often preferable to produce the monohydrate by one of the processes described on pp. 45-49.

Limited Market

Despite the simplicity of this recovery process, copperas manufacture cannot supply a universal solution to the pickle liquor problem, because of the limited market for the compound. Copperas and lime, and chlorinated copperas, are efficient coagulants for the treatment of water, sewage, and many industrial wastes. Expansion of this market, especially near centers of steel manufacture, is an attractive possibility. Unfortunately, copperas cannot be shipped long distances economically because 45% of its weight represents water.



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Fig 9

RECOVERY OF COPPERAS AND SULFURIC ACID

A variety of processes has been proposed for crystallizing copperas from spent pickle liquor and recovering the free acid for re-use in the picklers⁽¹⁾. These processes can be divided into three general types: cooling, plus addition of make-up acid to reduce the solubility of ferrous sulfate; evaporation of considerable water; and differential solubility.

Cooling Processes

The effect of sulfuric acid on the solubility of ferrous sulfate is an important factor in this type of process. Pickling is usually done at a temperature of 180°F. or higher, and cooling the spent liquor to atmospheric temperature will usually result in crystallization of some copperas. But the mother liquor would still contain a relatively high concentration of ferrous sulfate. The liquor would have to be cooled by refrigeration to a low temperature to remove enough ferrous sulfate to yield a recovered acid suitable for re-use in the picklers.

About the same effect can be obtained without cooling the liquor to a low temperature, however, by adding the required amount of make-up acid to the spent liquor before it is cooled. The effect of sulfuric acid in reducing the solubility of ferrous sulfate is illustrated in Fig. 10. Copperas is the solid phase in equilibrium with solutions whose composition falls on the lift of the transition curve, while monohydrate is in equilibrium in the region to the right (29).

Various improvements over the simple addition of make-up acid have resulted in greater efficiency. In one process the waste liquor is cooled to atmospheric temperature and the crystallized copperas is separated. Strong sulfuric acid is then added to the mother liquor until the concentration of free acid is 28%. This liquor is then cooled to 32° F. by mechanical refrigeration and a second crop of crystals is obtained. The second mother liquor is then diluted with water to a concentration of 18% sulfuric acid and returned to the pickling tank. (Fig. 11).

In another process a portion of the recovered copperas is dried to the monohydrate in a rotary kiln. The monohydrate is then dissolved in the spent liquor prior to cooling. This has the effect of removing water from the solution because each molecule of ferrous sulfate that crystallizes as copperas removes seven molecules of water from the solution.

Evaporation Processes

Among the processes that depend upon evaporation of water to recover free acid and copperas, the Butler-Little process (35) is well known because it has been operated on a commercial scale and received considerable publicity. The spent liquor is sprayed into the top of a high, lead-lined tower while air is blown in at the bottom. The countercurrent flow of air and liquor has the effect of vaporizing some of the water and cooling the liquid. Copperas crystallizes in the cone-shaped base of the tower. The crystals are separated by centrifugation and the mother liquor is returned to the picklers. Where live steam is used to heat the pickling bath, the rate of vaporization of water in the tower is inadequate to prevent accumulation of excessive water in the system.

The Simonson-Mantius process (26) concentrates waste pickle liquor in a vacuum evaporator until the free acid reaches 28%. The liquor is withdrawn and cooled, the copperas separated in a centrifuge, and the mother liquid returned to the pickling tanks. When detrimental impurities have accumulated to a harmful extent, the mother liquor from the first stage is transferred to a high-vacuum evaporator where the concentration of sulfuric acid is raised to 68-78% and practically all of the undesirable materials precipitate.

Although a number of modifications of the evaporation methods have been used, they do not differ in principle from these examples. As with other processes for recovering free acid, their economic aspects are likely to improve if the price of fresh acid increases as a result of the world-wide shortage of natural sulfur.

Differential Solubility

A somewhat different principle has been used to recover the free acid in pickle liquor whereby certain organic compounds can be employed to reduce the solubility of ferrous sulfate. A patent was issued to de Lattre(24) on a process for adding a fatty alcohol to waste pickle liquor to precipitate its copperas content. The copperas was separated in a centrifuge and the mother liquor was passed through a fractionating column to separate the alcohol from the free acid. This recovery method was studied thoroughly by the American Iron and Steel Institute Fellowship at Mellon Institute.

Certain water-soluble organic solvents have the property of reducing the solubility of moderately soluble inorganic salts in aqueous solution. A large number of solvents was investigated, and acetone was finally determined to be the most generally satisfactory agent for the purpose.

The laboratory work indicated that the unit operations involved would be rather simple in themselves.(22) Equal volumes of acetone and pickle liquor are mixed thoroughly; the finely crystalline copperas is separated in a basket centrifuge and the acetone is recovered from the mother liquor by fractionation. (Fig. 12) Practically all the free acid is recovered in the still bottoms which, when made up to pickling strength with fresh acid, will contain less than 2% of ferrous sulfate. A laboratory study of the free acid recovered in this process indicates that it is suitable for re-use in the picklers. Six pickling and recovery cycles were run in which the operations of batch pickling were simulated; there was no tendency for impurities to accumulate in the liquor. The recovered acid appeared to be the equivalent of fresh acid as a pickling agent.

This process has the advantage of recovering 95% of the ferrous sulfate and substantially all of the free acid in waste pickle liquor. The recovered acid solution contains a lower proportion of ferrous sulfate than similar solutions from refrigeration processes. On the other hand, the success of the process depends upon the recovery of at least 99.5% of the relatively expensive, highly flammable solvent.



SOLUBILITY OF FERROUS SULFATE IN ACID SOLUTIONS... The unusual feature is the maximum solubility at about 58°C.

Fig 11



DROOF PROCESS, MANUFACTURE OF COPPERAS AND RECOVERY OF FREE ACID FROM PICKLE LIQUOR BY COOLING ... Second cooling stage required because of unusual temperature -- Solubility characteristic of ferrous sulfate is shown in Fig 9.





RECOVERY OF FERROUS SULFATE MONOHYDRATE AND SULFURIC ACID

The advantages of ferrous sulfate monohydrate -- low water content, good storage properties, preferred form for sulfuric acid manufacture -- have led to a number of processes for preparing this compound from pickle liquor. The principles used by the different processes are (a) evaporation of the liquor, in which the free acid has been neutralized with scrap, in a directfired rotary dryer(3^4); (b) evaporation of the neutralized liquor in a spray dryer(3^0); (c) vacuum evaporation until the sulfuric acid concentration approaches 78%, when ferrous sulfate is completely insoluble(2^6); (d) heating the liquor under pressure to 300 to 400°F. and filtering the monohydrate without reducing temperature or pressure(37); (e) evaporation by submerged combustion (3); and (f) continuous circulation of the liquor through a direct-fired furnace, monohydrate removal equipment, and the pickling tanks(27).

The Martin process(27) was designed to operate continuously as an integral part of the pickling process. It had been assumed that a high concentration of ferrous sulfate in the bath inhibited pickling, but Dr. Martin's work disclosed that the pickling rate is unaffected by ferrous sulfate, even at the saturation level, if the free acid is maintained at 18-22% by volume and the temperature is held at 190-210°F. Based on this finding, spent liquor, at 18.5% free acid and 66 g. ferrous ion per liter, is continuously withdrawn from the last tank of a continuous strip pickler and pumped to an evaporator where it is combined with about five times its volume of recycle liquor from a crystallizer. The mixed liquor is sprayed into a stream of hot gases at 2000°F. in a suitable furnace. This combustion gas effects evaporation of water from the solution and is cooled to 215°F. The concentrated liquor is removed from the gas by a centrifugal separator and drains to a crystallizer. The gas from the separator is washed with rinse water from the pickler to scrub out any entrained acid. The liquor in the crystallizer is heated to 220°F. by superheated steam generated in the Petro-chem furnace. Fresh acid is added to the crystallizer to supply the acid consumed in pickling; this raises the acid concentration to about 32% by volume. Under these conditions ferrous sulfate monohydrate crystallizes, and the suspended crystals increase in size by being held in the crystallizer for about two hours. Clear acid solution is drawn off, of which part is recycled to the evaporator and part goes to a dilution tank. The crystal slurry is drawn from the crystallizer and separated from the acid solution in a centrifuge. The crystals are washed and dried. The strong acid and the wash waters are discharged to the dilution tank where the composition of the solution is adjusted to 23.5% acid and 14 g. ferrous ion per liter before being pumped to the first tank in the pickle line. The flow of solution in the pickler is concurrent with the strip. The temperature in the first tank is held at 205°F., and decreases through the remaining three tanks to 190°F. in the last one to increase successively the solubility of the monohydrate.

Properly balanced, this process provides continuous separation of ferrous sulfate from spent pickle liquor and maintains constant pickling conditions. Its disadvantage lies in high capital and operating costs, but development of a market for the superior quality monohydrate, if produced, would act as a partial offset.

Submerged Combustion Process

The Chemico process⁽³⁾ uses a submerged combustion burner to concentrate waste pickle liquor to precipitate ferrous sulfate monohydrate. In the pilot plant study, pickle liquor containing about 12% free acid and 20% ferrous sulfate was fed continuously to a cone-bottom, lead- and brick-lined steel tank equipped with a combustion dip pipe fired with light fuel oil. Evaporation maintained the acid concentration at 60 to 70% to cause precipitation of practically all the ferrous sulfate as the monohydrate. The slurry was continuously withdrawn to a rotary vacuum filter constructed of lead and covered with a plastic filter cloth. The pilot plant was designed to process 50 tons of liquor per day.

This process utilizes the efficiency of high-temperature, directflame evaporation and provides a method that is reported to be economical for recovering about 85% of the free acid in pickle liquor. The monohydrate could be processed to sulfuric acid and iron oxide, but such an operation would suffer from the disadvantages discussed in on pp. 50-51.

RECOVERY OF IRON OXIDE AND SULFURIC ACID

Conversion of spent pickle liquor into iron oxide and sulfuric acid is in effect the conversion of a spent material into products usable in a steel mill. Some of the processes that have been proposed or tested are as follows:

A Combination Dry-Roasting Process that has been operated successfully in another field, neutralizes the spent liquor with iron oxide and evaporates it to dryness in a direct-fired rotary kiln. The cinder is mixed with iron pyrite and roasted, and the purified kiln gas is converted to sulfuric acid in a vanadium contact plant.

Other Drying-Roasting Processes obtain sulfur dioxide by roasting a mixture of ferrous sulfate trihydrate with brown coal(33); drying copperas to the monohydrate and roasting it in a Herreshoff furnace; spray-drying neutralized liquor and roasting monohydrate in a special furnace to which a controlled amount of excess air is added to convert the sulfur dioxide to the trioxide through the catalytic effect of the hot, freshly formed iron oxide.

Sintering Process(3)

Ferrous sulfate monohydrate is mixed in a pug mill with 12% by weight of crushed coal plus some fine, sintered oxide. The mixture is extruded through a perforated plate to yield short, quarter-inch cylinders which are dried on a moving grate. The relatively soft pellets are converted to a hard agglomerate by heating, an operation known as sintering. Some of the coarse sinter is recycled to provide a bed for the pellets. This yields large chunks of semifused oxide suitable for blast furnace burden.

The wind box of the sintering machine is divided into two parts: one supplies a gas containing 7.5% sulfur dioxide that is suitable for a vanadium contact plant after being scrubbed, the other contains less than 0.1% sulfur dioxide and is used to dry the pellets.

Manufacture of Sulfuric Acid from spent pickle liquor, by one means or another, is feasible, but may be uneconomical. Sulfuric acid plants must be operated continuously and on a scale of not less than 50 to 75 tons of acid per day; otherwise, overhead and maintenance charges become excessive. Very few steel mills produce enough pickle liquor to justify an acid plant of this capacity.

Operation of a Cooperative Plant to serve a single steel-producing area might be considered. Unit shipping costs and other engineering problems stand in the way of this solution. Exhaustion of supplies of natural sulfur may, however, eventually alter the economics of acid manufacture from spent pickle liquor.

RECOVERY OF FERRIC SULFATE AND SULFURIC ACID

The autoxidation principle, patented in 1888, has attracted attention in recent years as a means for preparing ferric sulfate or sulfuric acid from spent pickle liquor⁽⁹⁾. Although the proposed processes differ in some particulars, they depend upon the catalytic air oxidation of a solution of sulfur dioxide and ferrous sulfate. Such a process can be controlled to produce either a strong solution of ferric sulfate or a 20% solution of sulfuric acid. It has been successfully operated in conjunction with a sewage-treatment plant to provide ferric sulfate solution for use as a coagulant. If operating costs could be kept low enough, this type of process would find application in certain areas.

Reaction rate

The Mellon Institute group investigated this type of process in a reactor they designed to improve the oxidation efficiency. A stream of sulfur dioxide and oxygen was dispersed in pickle liquor at 60° C. by a special impeller that caused a pronounced shearing action and thus distributed the gases as thin films. The process yielded ferric sulfate up to a concentration of 600 grams per liter (42% solution) with a low free acid content.

The oxidation rate is primarily a function of total iron con-- centration and temperature. It can be expressed by the equation:

$$dFe + + + /d0 = -0.0609 Fe + 1.92t^{0.413}$$

over the temperature range 47 to 80° C. dFe+++/dO represents the rate of formation of ferric iron in grams per minute; Fe is total iron in grams per liter; and t is degrees Centigrade. This equation shows that oxidation increases with temperature at a decreasing rate and that little would be gained by operating at a temperature above 80° C.





ELZI PROCESS FOR MANUFACTURE OF AMMONIUM SULFATE FROM PICKLE LIQUOR USING RAW COKE OVER GAS ... Ammonia is added to pickle liquor in two stages, following which air is added to insure complete removal of iron as the oxide.

RECOVERY OF IRON OXIDE AND AMMONIUM SULFATE

Combining spent pickle liquor with coke oven ammonia to produce ammonium sulfate and iron oxide is an obvious possibility that has been investigated⁽⁶⁾ The obstacles to the development of a feasible process were very great: difficulty of eliminating impurities in ammonia and pickle liquors to avoid contamination of the ammonium sulfate, separation of the hydrated iron oxides from the sulfate liquor, evaporation of large volumes of water, and lack of stoichiometric relations between pickle liquor and ammonia. Nevertheless, a number of processes were developed, some industrially, but none ever reached successful commercial operation, largely because of the costly equipment required, corrosion encountered and difficulty in producing an acceptable ammonium sulfate.

The Elzi $Process^{(8)}$ neutralizes the free acid in the spent pickle liquor with scrap iron; passes this liquor through a packed tower where it is scrubbed countercurrently with coke oven gas to raise the pH of the liquor to 7.0-7.5 by absorption of ammonia; raises the pH of the liquor to 8.0-8.5 in another packed tower with pure ammonia from the ammonia still; aerates the liquor in a third tower to oxidize the iron to ferric oxide; and filters off the oxide, which may be calcined to rouge or sintered for blast furnace burden. The filtrate may be evaporated to recover ammonium sulfate, or sent to the conventional ammonium sulfate saturators of the coke plant. (Fig. 13)

The Tiddy Process scrubs ammonia and hydrogen sulfide from coke oven gas with pickle liquor in two stages (36). The gas passes successively through a first and second chamber countercurrent to the flow of a feed liquor comprising pickle liquor and recycle liquor. (Fig. 14) The pickle liquor and recycle liquor enter the top of the second chamber and the liquor is pumped from the bottom of the second chamber to the top of the first chamber. The flow of coke oven gas is so regulated that the liquor leaving the first chamber will contain not less than 2.0 grams per liter of ferrous sulfate. The precipitate of ferrous oxide and ferrous sulfate is separated by decantation from the slurry flowing from the bottom of the first chamber, and part of the clear liquor is recycled to the stream of pickle liquor entering the second chamber. The ammonia content of the remainder of the clear liquor is increased to at least 0.5 gram per liter. This liquor is pumped to an aeration tower where its iron content is oxidized with air and precipitated. The precipitate is separated, and the liquor passes to an evaporator for recovery of ammonium sulfate. The oxide-sulfide sludge is sintered to a material suitable for charging to blast furnaces.





TIDDY PROCESS FOR MANUFACTURE OF AMMONIUM SULFATE FROM PICKLE LIQUOR USING RAW COKE OVER GAS ... Essentially a modification of the Elzi Process wherein the bulk of the iron precipitate is removed before aeration to insure complete iron removal.

Mellon Institute Pure Ammonia Process

In this $process^{(13)}$, purified ammonia and pickle liquor are fed continuously to a reactor of special design in which the precipitated ferrous hydroxide is oxidized under carefully controlled conditions to ferroso-ferric oxide; by this means the iron is precipitated completely. The magnetic iron oxide produced in this manner settles rapidly (95% in 5 minutes), and it can be separated from the ammonium sulfate liquor by continuous decantation. Separation of the iron oxide was the operation which defeated many of the previous processes. Pure ammonium sulfate is recovered by evaporation of the final clear liquor.

Maintenance of a reaction temperature above $75^{\circ}C.$, and a ratio of ferric to ferrous iron in the slurry of 2.5 to 3.5, is the key to successful operation of this process. The principal component of the slurry is ferrosoferric oxide. An elevated temperature is essential to formation of an oxide that settles well. At even a few degrees below $75^{\circ}C.$ the settling rate falls off appreciably; higher temperatures have little effect. Ferroso-ferric oxide, which may be represented by the formula Fe₂O₃.FeO, has a ferric-ferrous ratio of 2.0. A minimum ratio of 2.5 is recommended to insure complete precipitation of all the iron in the pickle liquor; at ratios much above 3.5 the settling rate decreases. In actual practice the operation is easy to control. The ferric-ferrous ratio can be determined analytically by a simple procedure (see Appendix II), or the progress of the reaction can be followed by observing the settling rate of the slurry and determining the presence or absence of soluble iron in the supernatant liquor.

Pilot plant studies have demonstrated the technical practicability of the process. Its obvious economic advantage lies in the use of waste sulfate ion to produce ammonium sulfate. But the process would have the effect of increasing the world supply of ammonium sulfate. Although the demand for this compound as a fertilizer component is currently very high, there is nothing to assure a similar condition in the future.

Mellon Institute Coke Oven Ammonia Process

A process based on direct treatment of coke oven gas with pickle liquor would have several advantages. Such a process was developed with coke oven ammonia liquor fortified with additional cyanide and sulfate, to determine the maximum limits of these impurities for production of pure ammonium sulfate. The process was then operated with waste pickle liquor that had been used to scrub coke oven gas.

The process was an outgrowth of the pure ammonia-pickle liquor process described above. When an attempt was made to adapt that process to a material containing sulfides, the ferrous sulfide that precipitated settled poorly and was difficult to filter. This was overcome by carrying oxidation of the precipitate to ferric oxide, which settled and filtered very well. This step also caused much of the sulfur that had been combined with the iron to separate as elemental sulfur which could be recovered by froth flotation or solvent extraction. The cyanides were removed in combination with the iron oxide sludge. This process not only saves the sulfuric acid now used in the ammonia saturators, but it reduces the sulfur in the coke oven gas, thereby making it a more desirable fuel for many steel mill purposes. It has been demonstrated that pure ammonium sulfate can be prepared from gas containing a considerably higher concentration of sulfide and cyanides than is normally present. The cyanides can be completely recovered (as ferrocyanide) from the sludge by extraction with caustic soda.

Pickle liquor and coke oven ammonia are rarely in stoichiometric balance; usually there is a substantial deficiency of the former. This means that existing ammonia saturators would have to be retained to remove the surplus ammonia. Where pickle liquor and ammonia are in balance, the liquor will usually contain only enough iron to combine with about half the hydrogen sulfide in the gas. In such cases, supplemental sulfide removal equipment would have to be operated where a low concentration in the gas is essential. Coke ovens and pickling shops often are not close enough to each other to avoid costly pickle liquor transport equipment. For sound economic evaluation the process would have to be operated on a pilot scale at a steel mill. This has not yet been done. The process may prove to be economically feasible, but further plant-scale investigation is necessary.

MANUFACTURE OF CONSTRUCTION MATERIAL

Ferron, a building material with interesting possibilities, has been made from the sludge produced when pickle liquor is neutralized with lime under carefully controlled conditions (31). The sludge is filtered in a plate-and-frame press and the plastic material is blended with fillers in a pug mill from which it is extruded as long bars or other shapes. It has also been formed into sheets in a hydraulic press. The formed material is dried at $175^{\circ}F$. When dried, it is no longer plastic and can be sawed or machined.

Uses for Ferron

Ferron plasterboard is reported to be equal in physical properties to similar products made from gypsum. It is fireproof and is said to have good acoustic qualities. Shingles have been made by incorporating an asphalt emulsion with the sludge; performance tests have shown them to be wholly satisfactory. The slight excess of lime in the sludge inhibits corrosion of the nails used to attach them to a building. Granulated Ferron is said to be a good absorbent for removing hydrogen sulfide from gases.

Fig 15



PRODUCTION OF MANGANESE CONCENTRATE FROM LEAN ORE ... Manganese content of ore is dissolved by pickle liquor; iron and manganese are precipitated at different pH levels. Gypsum is a by-product.

EXTRACTION OF MANGANESE CONCENTRATE FROM LEAN ORE

This country has large deposits of low grade manganese ores, but almost none of sufficiently high grade for direct conversion to ferromanganese, an essential product required for manufacturing steel. The shortage of manganese was acute in the early days of World War II. A process(14) was developed at Mellon Institute making use of the reducing property of ferrous sulfate to concentrate manganese in low-quality oxide ores.

Technique

Low grade ore is ground to -60 mesh, mixed with a small excess of pickle liquor, and the gangue separated by filtration. The clear extract consists of manganous and ferric sulfates, plus a small amount of ferrous sulfate. The sulfates are converted to chlorides by treatment with calcium chloride, and the gypsum, CaSO₄.2H₂O, which precipitates can be recovered as a compound of high purity. The ferric iron in the filtrate is precipitated at a controlled pH by adding finely divided calcium carbonate. The filtrate is treated with lime slurry to precipitate the manganese, which is filtered off, washed, and dried as the main product. The filtrate from this step is a solution of calcium chloride its volume is reduced by evaporation and the liquor returned to the process (Fig. 15).

Results

This process produces a manganese concentrate containing upwards of 60% manganese and two by-products of low value. Its principal disadvantage is one of geography; most of the suitable manganese ores are mined at a great distance from the centers of steel manufacture.

Current research on this process indicates that a solution of ferrous sulfate containing no free acid can be used to extract the manganese and that the technology involved can be simplified. These developments should improve the economy of the process and increase its usefulness.



RECOVERY OF MAGNESIA FROM DOLOMITE USING PICKLE LIQUOR pH control effects separation of gypsum, iron and magnesia.

EXTRACTION OF MAGNESIA FROM DOLOMITE

A simple process was evolved at Mellon Institute for recovery of magnesia from dolomite using spent pickle liquor (Fig. 16).

Technique

The sulfates are converted to chlorides by treatment with a concentrated solution of calcium chloride at about 75° C., which temperature causes the calcium sulfate to precipitate in an easily filterable form and avoids its contamination with iron. The gypsum, CaSO4.2H₂O, is filtered off. The iron is precipitated from the chloride solution by treatment with a slurry of dolomitic lime, and the precipitate is separated by filtration. This separation is possible because ferrous iron can be completely precipitated at a pH of about 9, whereas magnesia does not precipitate until the pH rises to above 10.5. The separation can be made more efficient by providing aeration to oxidize the iron and thus lower the pH required for precipitation. More dolomitic lime slurry is then added to the clear filtrate to precipitate the magnesia. The product is filtered off and washed. The calcium chloride brine remaining is evaporated and recycled to convert more pickle liquor to a solution of chlorides.

Results

In the laboratory, magnesias of 91 to 94% purity were prepared by this process. The chief contaminant of the magnesia was calcium oxide, but this compound could be leached with water to improve the quality of the principal product. The hydrated iron oxide, which is precipitated in the iron removal step, has a high sulfur content that cannot be reduced without impairing the quality of the magnesia. Evaporation of the large volume of wash water required for the recovery of calcium chloride is a disadvantage.

MISCELLANEOUS PROCESSES

A number of processes have been proposed that have not found commercial application for various reasons. These include:

Electrolytic Iron

Several processes have been proposed for the recovery of iron from pickle liquor by electrolysis⁽⁵⁾, but none has been notably successful. Ferrous iron tends to oxidize and precipitate basic salts. Frequent regulation of the acidity of the bath is necessary to avoid this tendency and maintain a high cell efficiency. The cost of producing electrolytic iron requires a premium price for the product. Production of silicoirons and alloys with low hysteresis losses have discouraged the development of electrolytic iron installations.

Iron Powder

The increased use of various metal powders for use in the operations of powder metallurgy has drawn the attention of several investigators to the iron oxide obtainable from pickle liquor as a raw material for reduction. It has been predicted that the market for iron powder could be extended considerably, if a product of proper quality could be produced at a price appreciably below the current market. Preparation of the oxide in suitable form for reduction and sources of cheap hydrogen have hindered development of a sound process.

Iron Oxide Pigments

Various natural iron oxides have been used as pigments since ancient times and similar products are manufactured by decomposing copperas under controlled conditions (10). No special problems are involved where the pigments are produced by those skilled in the art, but the consumption of these products is relatively small in comparison with the total amount of waste pickle liquor available.

Iron Sulfates in Cement

The setting time of Portland cement is regulated by grinding 2 to 3% of gypsum, $CaSO_4.2H_2O$, with the cement clinker. Laboratory investigation(21) at Mellon Institute has indicated that iron sulfate, on an SO_3 basis, can be substituted for gypsum. Experimental cements containing iron sulfate compared favorably with commercial Portland cements in setting time and in tensile and compressive strengths. Test briquets made from samples of the experimental cements which had been stored for five years showed no appreciable diminution in strength. If this use for ferrous sulfate were adopted generally, it would consume more of the compound than is produced as waste pickle liquor.

There are, unfortunately, a number of serious drawbacks to this apparently simple method of utilizing pickle liquor. The procedure has not been studied on a commercial scale. Until this is done, there is no guarantee that the laboratory results can be duplicated in practice. Although the pale brown color of cement containing iron sulfate would be desirable for highway construction to reduce glare, contractors and consumers would have to be converted to the use of the new material. Amendment of the specifications of the American Society for Testing Materials would be necessary before the substitution would be permitted for certain applications. The most significant objection, however, is the improbability that sulfate as copperas could be purchased at as low a price as sulfate in the form of gypsum.

Ferric Chloride and Sodium Sulfate

The desirability of converting the iron in spent pickle liquor into compounds more valuable than copperas led to the development at Mellon Institute of a feasible process for producing saturated ferric chloride solution and pure anhydrous sodium sulfate. When the spent liquor is treated with an excess of sodium chloride, a double salt of iron and sodium sulfate precipitates. Glauber's salt, Na2SO4.10 H2O, is seperated from the mixture by successive crystallizations. During these operations, a ferrous chloride solution is produced from which a small amount of residual sulfate is precipitated by addition of calcium chloride. The ferrous chloride solution is chlorinated and evaporated to a 60% solution of ferric chloride. At this concentration practically all of the excess sodium chloride precipitates; it is filtered off and returned to the process. At 60°C. Glauber's salt melts in its water of crystallization and precipitates anhydrous sodium sulfate. The sodium sulfate is filtered off and the mother liquor recycled.

This is a practicable process for producing a saturated solution (60%) of ferric chloride, and anhydrous sodium sulfate containing not more than 0.5% of iron and 0.15% of sodium chloride. The process has the disadvantage of requiring a number of filtrations and refrigerations which must be carefully controlled for best results. The demand for pure sodium sulfate and the increasing usefulness of ferric chloride may, in time, improve the commercial potentiality of the process.

Ferric Phosphate

The Coleman process⁽⁴⁾ was developed to recover values from acid mine drainage, waste pickle liquor and other acidic wastes by treatment with phosphate rock. Pickle liquor, preferably containing 10% or more of acid equivalent, is treated with ground phosphate rock in a series of tanks until reaction is complete according to the general equation:

6FeS04 + 6H2S04 + 3Ca3(P04)2 + 18H20 -> 9CaS04.2H20 + 3FeS04 + Fe3(P04)2+ 4H3P04

Q. 1

The calcium sulfate is filtered off and sent to a dump. The filtrate is treated with soda ash in a tank with a paddle stirrer and air agitation until the reaction, as expressed by the equation:

 $3FeSO_4 + Fe_3(PO_4)_2 + 4H_3PO_4 + 3Na_2CO_3 + 3/2 O_2 \longrightarrow 3Na_2SO_4 + 6FePO_4 + 3CO_2 + 6H_2O_3$

is complete. The ferric phosphate is filtered off and dried; the filtrate sent to the sewer. Originally planned to provide a coagulant for chemical treatment of sewage, a sufficiently large market could not be developed to justify a commercial installation.

The Sulfide-Sulfate Cycle

In a process patented by Rosenstein(32) to recover sulfuric acid from a variety of waste acid liquors, the waste is diluted to a maximum of 20% sulfuric acid and treated in a covered reactor with barium sulfide, BaS. The evolved hydrogen sulfide is oxidized to sulfuric acid in a separate plant. These reactions are represented by the equations:

> BaS + $H_2SO_4 \longrightarrow BaSO_4 + H_2S$ $H_2S + 2O_2 \longrightarrow H_2SO_4$

The barium sulfate is settled and dewatered further on a rotary vacuum filter. Supernatant and filtrate are run to the sewer. The barium sulfate plus the make-up barytes are mixed with a calculated quantity of fine-ground coal or coke and roasted in a reducing furnace to produce the reaction:

BaSO4 + 4C -> BaS + 4CO

The resulting black ash is leached with water and the solution of barium sulfide is pumped to the reactor. The residue in the leach tank is hauled to a dump. This process has not proved to be practical.

APPENDIX I - HOW TO USE BASICITY FACTOR

This section includes a number of analytical procedures that will be found helpful in problems involving pickle liquor disposal or neutralization.

Definition of Basicity Factor

The basicity factor(15) of an alkaline agent is a measure of the available alkalinity of the agent that avoids dependence on chemical analysis. This factor is of particular utility in evaluating the available alkalinity of limes, limestones and related materials, because chemical analysis of these substances is time-consuming and the results give limited information about their reactivity. The numerical value of the basicity factors cited here represents the grams of equivalent calcium oxide per gram of material. Where waste liquors are to be neutralized, the actual composition of the alkaline substance usually is not particularly important as long as its alkalinity can be related to some reference compound. Equivalent calcium oxide was chosen as the logical reference compound for pickle liquor treatment.

When limestone is calcined, some of the calcium and magnesium oxides may combine with silica, alumina and iron oxides to form compositions that are insoluble even in moderately concentrated acids; the neutralizing value of the substance is thereby reduced. On the other hand, certain complex calcium and magnesium silicates in limestone may decompose on calcination. Chemical analysis would not ordinarily distinguish between the available and unavailable alkaline components. The temperature of calcination and the particle size of the final product are important factors governing the availability of the neutralizing value of a lime.

The method for determining basicity factors reflects the value of the substance as a neutralizing agent under the conditions of use, and the procedure is quite simple. A sample of the material is heated with an excess of acid; after the proper interval of time the excess acid remaining is titrated, and the net acid consumed is calculated to grams of calcium oxide per gram of sample. The detailed procedure for lime is given below.

Determining Basicity Factor

Using a weighing bottle, weigh accurately about 1.3 grams of lime and transfer the sample to a small porcelain crucible. Place the crucible upright in a 250-ml. beaker containing 15 ml. water. Cover the beaker, heat the water to boiling, and tip the crucible to fill it with the hot water. Allow to stand for several minutes to slake the lime completely. Scrub the crucible with a rubber policeman, wash and remove it, run in from a burette the quantity of 0.5 N sulfuric acid required to react with the lime, then add 30-35 ml. in excess. Wash the mixture into an Erlenmeyer flask, boil for 15 min., cool to room temperature, and titrate with 0.5 N sodium hydroxide to a phenolphthalein endpoint. The boiling period suggested here is ample for most limes to develop their full basicity with sulfuric acid. The procedure for limestones is similar, except that a larger sample (about 2.5 grams) is used and the slaking step can be eliminated.

Calculation	0.028	(ml.	H2SO4	x N)	-	(ml.	NaOH	x	N)	g.	equi	valent
			g.	samo	le					Ca	0 per	gram

This method can be used with any common acid, and the choice of acid should be governed by the application intended. Basicity factors determined for a given boiling period obviously will vary with the same strengths of different acids and different strengths of the same acid unless the full basicity is obtained. In the procedure given above, it was desired to obtain the full basicity of the sample, but it is evident that the method provides means for establishing relative reactivities under any chosen set of conditions. Basicity factors for representative limestones, quicklimes and hydrated limes will approximate the values in Table VIII.

Material	g. CaO/g.
High calcium limestone	0.49
High calcium quicklime	0.94
High calcium hydrate	0.71
Dolomitic limestone	0.56
Dolomitic quicklime	1.11
Dolomitic hydrate	0.92

TABLE VIII. REPRESENTATIVE BASICITY FACTORS

Where use of limestone is contemplated, the important relation between particle size and reaction rate must be recognized, and this is illustrated by the data in Table IX. In each case, samples of good quality 30-mesh high calcium limestone were ground until the whole sample passed a particular screen.

Basicit	y Factors	of Samples G	fround to Pas	s Mesh No.
30	65	80	100	200
0.4443 0.4571 0.4736 0.4855	0.4572 0.4879 0.5088 0.5211 0.5249	0.4798 0.5030 0.5170 0.5229	0.4874 0.5153 0.5244	0.5231
	Basicit 30 0.4443 0.4571 0.4736 0.4855	Basicity Factors 30 65 0.4443 0.4572 0.4571 0.4879 0.4736 0.5088 0.4855 0.5211 0.5249 0.4058	Basicity Factors of Samples 0 30 65 80 0.4443 0.4572 0.4798 0.4571 0.4879 0.5030 0.4736 0.5088 0.5170 0.4855 0.5211 0.5229 0.5249	Basicity Factors of Samples Ground to Pas 30 65 80 100 0.4443 0.4572 0.4798 0.4874 0.4571 0.4879 0.5030 0.5153 0.4736 0.5088 0.5170 0.5244 0.4855 0.5211 0.5229 - 0.5249 0.4058

TABLE IX. EFFECT OF PARTICLE SIZE ON REACTIVITY OF LIMESTONE

Definition of Acid Value

Calcium hydroxide (slaked or hydrated lime) is only slightly soluble in water, but that which dissolves is completely ionized to calcium and hydroxyl ions. When lime slurry is mixed with pickle liquor the hydroxyl ions combine rapidly with hydrogen and/or iron ions, permitting more lime to dissolve. For every hydroxyl ion that reacts, an equivalent amount of calcium sulfate is formed; this compound largely precipitates, due to its limited solubility. Complete treatment of pickle liquor by neutralization may therefore be considered to be a union of calcium and sulfate ions to form calcium sulfate. To compute the amount of alkaline agent required to neutralize a given quantity of liquor, it is thus necessary to know only its total sulfate content.

Accurate chemical analysis of pickle liquor requires considerable time, but its acid value(15), or total sulfate content, can be determined with an accuracy of 0.2 per cent in 15 to 20 minutes by a rather simple procedure.

Determining Acid Value

Pipette accurately 5 ml.* of the sulfate liquor into 50 ml. of distilled water in a 250 ml. beaker. Run in from a burette 25-30 ml. of 0.5 N sodium hydroxide in excess of that required for complete reaction. Heat to boiling for 2-3 minutes, stirring to avoid loss by bumping. Prepare a filter by placing a No. 42 Whatman (or equivalent) filter paper in a small Buchner funnel, moisten, and apply vacuum. Pour about 10 ml. of a thin slurry of acid-washed asbestos on the filter, and rotate the funnel rapidly to throw

^{*} Size of sample will be governed by the strength of the liquor. For strong liquors a 1 ml. sample should suffice; in this case, a 10 ml. sample should be diluted to 100 ml. in a volumetric flask and a 10 ml. aliquot taken for analysis.



NOMOGRAPH FOR SPENT ACID TREATMENT ... Connect scales A and B with a straightedge; read pounds of alkaline agent required per gallon of spent acid on scale C.
the fibers to the edges of the paper to form a good seal. Turn off vacuum and pour the boiling mixture on the filter. Immediately begin applying vacuum gradually, taking 15-20 seconds to turn it on full to prevent the finelydivided precipitate from passing the filter.** Wash the residue with four 10 ml. portions of water; this will usually be sufficient to recover all of the excess sodium hydroxide, but the final wash may be tested for alkali with phenolphthalein paper. Add a few drops of phenolphthalein indicator solution and titrate with 0.5 N sulfuric acid to disappearance of the pink color.

 $\frac{\text{Calculation}}{\text{ml. NaOH x N}} = \text{g. equivalent SO4 per liter}$

Simple Calculation of Alkaline Dosage

The nomograph shown in Figure 17 provides means for rapid estimation of the amount of alkaline material required for complete treatment of a given pickle liquor⁽¹⁵⁾. It was constructed on the assumption that the agitation would be adequate to insure attainment of the full basicity of the neutralizing agent under the conditions for which the basicity was determined.

For various reasons, the reaction of pickle liquor with an alkaline agent is quite complex, and the pH of a slurry of lime and pickle liquor is an unsatisfactory indicator of completion of the reaction. It is more or less customary in industry to add milk of lime to pickle liquor until a sample of the slurry is alkaline to phenolphthalein. This procedure may result in underor over-treatment, depending on the rate of lime addition, degree of agitation, strength of the liquor, temperature, reactivity of the lime, and other factors. The best way to insure complete treatment with maximum lime efficiency is to use the basicity factor-acid value relation.

 $\frac{48 \text{ (ml. NaOH x N)} - 2 \text{ (ml. H}_2SO_4 \text{ x N)}}{\text{ml. sample}} = \text{g. equivalent SO_4 per liter}$

^{**} Alternatively, the mixture may be washed into a 100 ml. volumetric flask, cooled to 25°C., filled to the mark with distilled water, mixed, and allowed to settle. A 50 ml. aliquot of the supernatant is pipetted to a flask for back titration. The result is calculated:

APPENDIX II - ANALYTICAL PROCEDURES FOR OPERATORS

Descriptions of analytical procedures that may be helpful to operators are:

Ferric-Ferrous Ratio

Determination of the ratio of ferric to ferrous iron provides a useful means for controlling processes involving magnetic iron oxide, and it may be helpful in other instances. The determination can be made rapidly by the following method:

Heat about 10 ml. of well-mixed slurry with 10 ml. of concentrated hydrochloric acid until dissolved, and dilute to about 25 ml. with water. Pipette 10 ml. of this solution into a beaker, add 10 ml. of titrating solution, and titrate with 0.1 N potassium permanganate to a definite pink color. This gives the ferrous iron content. Pipette another 10 ml. portion of the solution into a small beaker and add permanganate solution dropwise until a permanent pink or brownish color appears. Heat nearly to boiling, add stannous chloride solution dropwise with stirring until the yellow color of ferric chloride is discharged, then add one drop more. Wash down the inside of the beaker, cool in ice-water and add 10 ml. of saturated mercuric chloride solution at one stroke. Allow to stand for a few minutes, then transfer to 400 ml. or cool water to which 10 ml. of titration solution has been added. The mixture should contain a white, silky precipitate; if the precipitate is gray or black, the determination must be rerun because too much stannous chloride has been added. Titrate with 0.1 N permanganate to a definite pink color. This gives the total iron; subtraction of the ferrous iron gives ferric, and division of ferric by ferrous gives the ratio.

The iron titer of the permanganate is found from the formula:

Iron titer = 0.05585 x Normality of permanganate.

Then, for each titration, ml. permanganate x iron titer = grams of iron in the 10 ml. portions.

Ferrous Iron

To determine the ferrous iron content of strong sulfate pickle liquor, pipette 10 ml.* into a 100 ml. volumetric flask, make up to the mark with water, mix, pipette 10 ml. to a beaker, add 10 ml. of 10 per cent sulfuric acid, and titrate to a pink color with 0.1 N permanganate. Then:

ml. permanganate x iron titer x 1000 = grams ferrous iron per liter.

* For rinse water or weak liquor a proportionately larger sample should be used.

Iron In Supernatants

Make a portion of clear supernatant alkaline with ammonia and add a few drops of hydrogen peroxide. A brown coloration or precipitate indicates iron in solution. This test is sensitive to about 5 parts per million. Depth of color or amount of precipitate provides a rough measure of the quantity of iron in solution.

REAGENTS

Certain special solutions are required for carrying out the analytical procedures. These are:

Mercuric Chloride

Prepare a saturated solution of mercuric chloride, HgCl₂, in distilled water. It is desirable to have a small amount of undissolved salt in the reagent bottle at all times to insure saturation.

Standard Potassium Permanganate

Dissolve 3.2 grams of C.P. potassium permanganate, KMnO4, in a liter of distilled water, boil for 10-15 minutes and allow to cool overnight. Filter through a layer of acid-washed asbestos and standardize against sodium oxalate, as follows:

Weigh accurately 0.3 g. of sodium oxalate, $Na_2C_2O_4$, (Bureau of Standards Sample 40d) and transfer to a dry 600 ml. beaker. Add 250 ml. dilute sulfuric acid (5:95) previously boiled for 10-15 minutes and cooled to $27^{\circ} \pm 3^{\circ}C$. Stir until the salt is dissolved. Add 39-40 ml. of the permanganate solution from a burette while stirring slowly. Let stand until the red color disappears (about 45 seconds), heat to 55-60°C. and add permanganate to a pink color that persists for 30 seconds. Toward the end of the titration, each drop of permanganate must be allowed to decolorize before adding another. The solution should be stored in a glass-stoppered bottle covered with several layers of dark paper; properly prepared and protected, it will be stable for several months, but its normality should be checked from time to time. The normality is calculated from the formula:

$$N = \frac{g. \text{ oxalate}}{0.067 \text{ x ml. permanganate}}$$

Standard Sodium Hydroxide

Weigh out 23 g. of sodium hydroxide, NaOH, dissolve in water, pour into a bottle, dilute to approximately a liter, and shake thoroughly. The bottle should be closed with a rubber stopper. The normality is determined by titration against standard sulfuric acid, as described below.

Stannous Chloride Solution

Dissolve 150 g. of stannous chloride, SnCl₂.2H₂O, in 300 ml. of concentration hydrochloric acid and dilute to 1000 ml. with distilled water.

Standard Sulfuric Acid

Dilute 2.8 ml. of concentrated sulfuric acid, H_2SO_4 , to 1000 ml. and standardize as follows:

Weigh accurately about 0.2 g. of <u>pure</u> sodium carbonate, dissolve in 100 ml. of distilled water, add 3 drops of a 0.02 per cent solution of methyl orange, and titrate to the first permanent pink color that can be duplicated readily. The normality of the solution is calculated from the formula:

 $N = \frac{g. \text{ carbonate}}{0.053 \text{ x ml. acid}}$

The sodium hydroxide should be standardized against the acid by diluting 30 ml. of the hydroxide to 100 ml. with distilled water, adding 3 drops of methyl orange, and titrating to the first permanent pink color. The normality of the alkali is calculated from the formula:

N (alkali) = $\frac{N (acid) \times ml. acid}{ml. alkali}$

Titrating Solution

Dissolve 200 g. of manganous sulfate, $MnSO_4.4H_2O$, in 1000 ml. of distilled water, and add a cooled mixture of 400 ml. concentrated sulfuric acid, 1200 ml. distilled water, and 400 ml. syrupy phosphoric acid.

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