# Experiences with Acid Mine-water Drainage in Tri-State Field

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## INTRODUCTION

ACID mine-water drainage is a serious problem with many mines in the Tri-State zinc and lead mining district. Particularly is this true when large volumes must be considered in unwatering old mines that have refilled with water which has dissolved the products of oxidation and has become chalybeate in character.

The experiences discussed in this paper have to do specifically with the unwatering of a comparatively small area west of the town of Baxter Springs, Kans., where the pumping job was complicated by water of this type and where the extremely high sulphate content particularly effected that phase of mine drainage having to do with stream pollution.

## LOCATION, GEOLOGY AND HISTORY

The Baxter Springs area of the Tri-State mining field is situated just west of the town of Baxter Springs and is a northeasterly extension of the main mineralized zones of the Oklahoma part of the district (Fig 1).

The mining area is traversed with well defined shear zones which provide easy circulation of ground waters and the ore bodies are found along these shear zones as localized enrichments wherever the structural conditions are favorable (Fig 2). The ore-bearing strata is Mississippian with an overlain capping of shale of Pennsylvanian age. This shale strata carries much pyrite and marcasite at its base and undoubtedly was a contributing factor to the subsequent high iron content of the water.

The area originally contained a sulphide water which discharged as an artesian flow in springs within the town and gave Baxter Springs its name. These springs were famed for many years for their mineral water.

This original sulphide water was first removed about 1917 and active mining was carried on west of the town during subsequent high metal price periods. Many small mines were opened, with each localized enrichment becoming a separate mine. During the depression mining ceased and all mines in the west Baxter area were allowed to flood. No serious effort was made to again unwater until higher prices caused from the demand for metal for World War II once more focused attention on this part of the field.

## ORIGINAL MINING RESULTS IN OXIDATION

As plans for unwatering progressed, it soon developed that the mine-water pools had become strongly acid in character and carried large amounts of sulphates in solution. This occurred in the following way. When the original sulphide water was removed, shafts sunk, and mining carried on over a number of years, ferrous sulphate was formed by the spontaneous oxidation of the pyrite beds in contact with air admitted through churn-drill holes and mine openings. These products of oxidation can be seen today in the old mines of the district as crusts of crystalline sulphates

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on the walls of stopes and as stalagtites and stalagmites formed under roof drips. Ferrous sulphate predominated, but large amounts of other sulphates were precipitated as oxidation products of the alkaline carbonates and bicarbonates. The oxidation covered a large area because of the fact that the shear zones were very open and permitted easy circulation of air during the period of mining. With the cessation of mining operations during the depression the entire area refilled with water and the accumulated sulphates formed by this oxidation were dissolved. As the water table rose, a large amount of ferric sulphate was also formed from the oxidation of the ferrous sulphate together with the basic ferric sulphate.

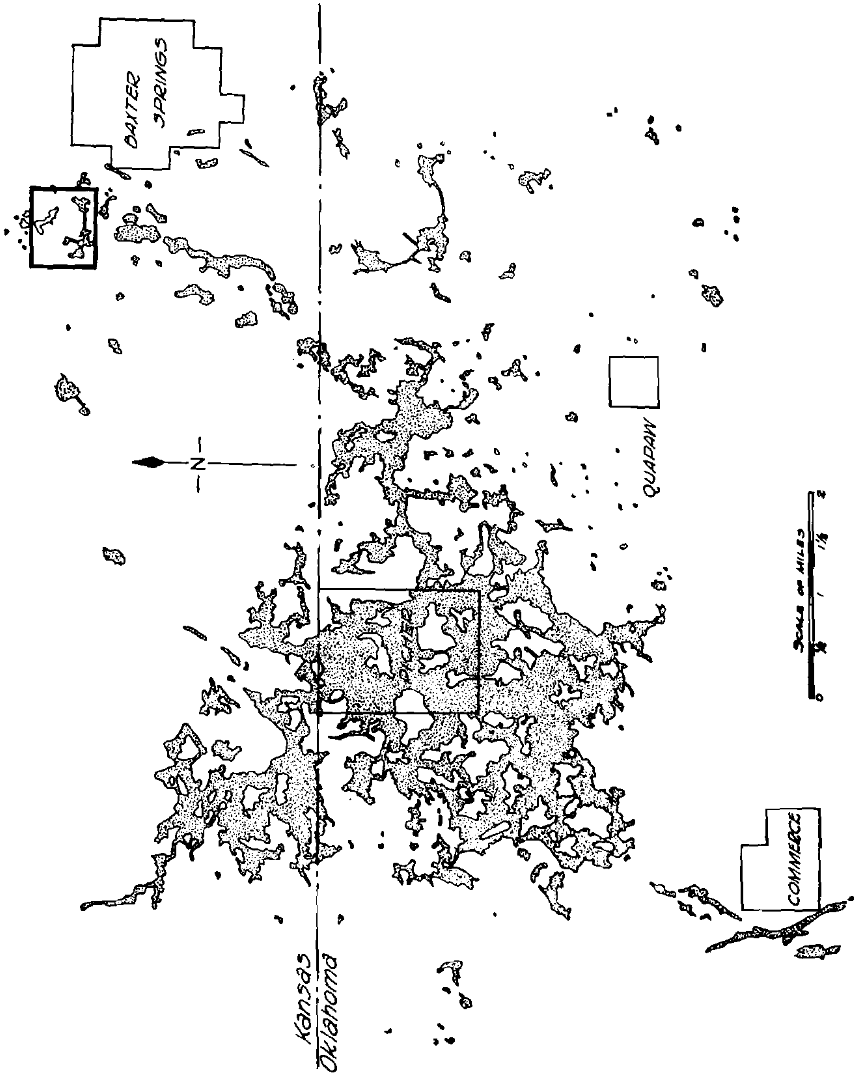

FIG 1—TRI-STATE KANSAS-OKLAHOMA AREA.

$$6FeSO_4 + 3O + 3H_2O \rightleftarrows 2Fe_3(SO_4)_3(OH)_3 \rightleftarrows 2Fe_2(SO_4)_3 + 2Fe(OH)_3.$$

The action of this ferric sulphate took iron into further solution from the pyrite when contact was made with the pyrite beds, and more ferrous sulphate was formed.

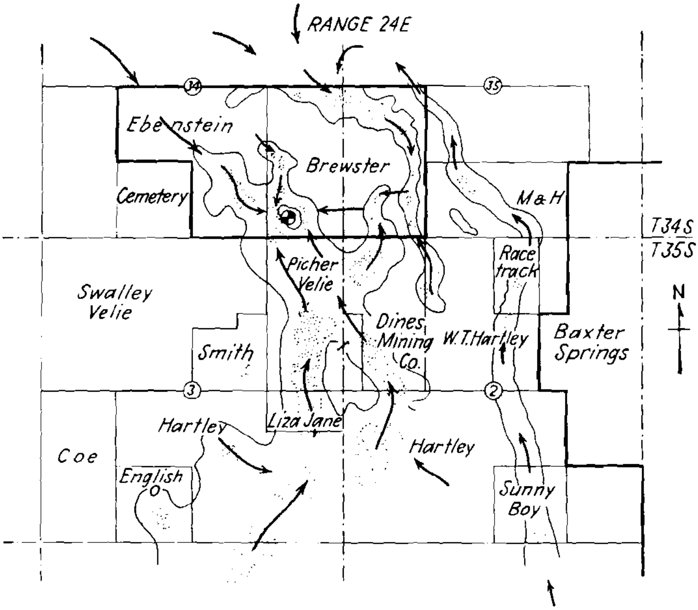

Fig 2—Shear zones showing ore bodies.

$$Fe_2(SO_4)_3 + FeS_2 \rightleftarrows 3FeSO_4 + 2S$$
$$2S + 6Fe_2(SO_4)_3 + 8H_2O \rightleftarrows 12FeSO_4 + 8H_2SO_4$$
$$Fe_2(SO_4)_3 + H_2O \rightleftarrows 2FeSO_4 + H_2SO_4 + O$$
$$Fe_2(SO_4)_3 + Fe \rightarrow 3FeSO_4$$

Since iron predominated, only a few of the iron reactions are given, but similar reaction formulas can be written for most of the other heavy metals.

## THEORY OF ELECTROLYTIC DISSOCIATION APPLICABLE

According to the theory of electrolytic dissociation, water, or any liquid containing water in good measure, contains free positively charged hydrogen or (H) ions and negatively charged hydroxyl (OH) ions. When these are in balance, the solution is said to be neutral and have a pH value of 7.0; i.e. the equality of the (H) ion and the (OH) ion concentration occurs at pH 7.0. Decinormal hydrochloric acid has a pH of 1.04, is completely ionized and contains one decigram of (H) ion. On the other end decinormal sodium hydroxide has a pH of 13.07.

An acid, therefore, is any substance capable of supplying to its solution hydrogen bearing a positive-electric charge and the expression of the intensity factor is the hydrogen-ion concentration, or pH. Thus the acidity of a natural water represents the content of free carbon dioxide, mineral acids, and salts, especially sulphates of iron and aluminum, which hydrolyze easily to given (H) ions.

Referring to Table 1 you will see that the mine-water analysis shows a high content of carbon dioxide and bicarbonates as $(HCO_3)_2$, as well as extremely high values

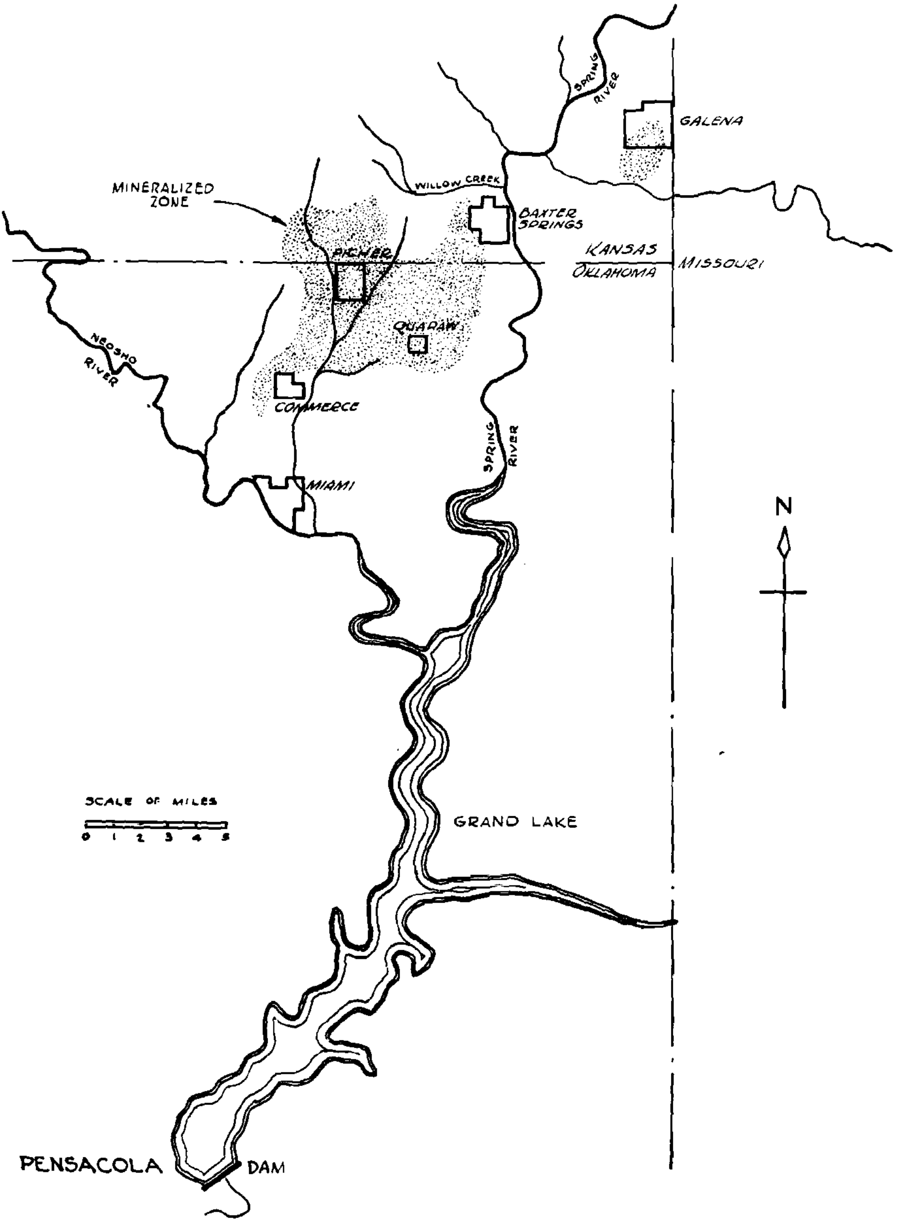

FIG 3—TRI-STATE MINING AREA DRAINAGE BASIN.

in the mineral acids and salts, particularly those of iron, which show as sulphates and all of which hydrolyze easily to positively charged (H) ions.

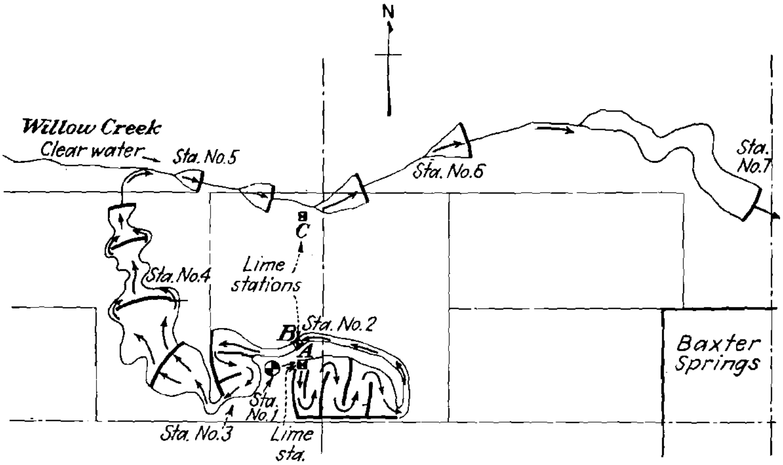

FIG 4—PLAN OF LIME-TREATMENT CIRCUIT WITH SETTLING BASINS AND LIME STATIONS.

All this spelled acid water and it is not surprising that an analysis shows the hydrogen-ion concentration at a pH of 2.45.

## STREAM POLLUTION PROBLEM

It was necessary to pump a large pool of this type water in order to unwater the mining area, and it was evident that if this water was discharged into stream drainage without treatment, a serious stream pollution would be created. Not only would it have detrimental effects on the use of Spring River from a recreational standpoint but it would also bear on the fishery problems in the Pensacola Dam Impoundment of the Grand River into which drainage would flow via Spring River (Fig 3). The effect of high concentrations of this type of water would be severe on fish life because of the acidity, the toxic metals in solution, the turbidity which would be created by the precipitates and the impoverishment of the dissolved oxygen of the river waters by the oxidation of the ferric iron. Based on these four points, therefore, our object was to discharge the mine water into Spring River so as to prevent undue change in the chemical quality of the river water.

TABLE 1—*Assay of Mine Water*[a]

| Constituents | Value | In Ppm |
|---|---|---|
| Ferrous iron | | 6,510 |
| Ferric iron | | 265 |
| Calcium | | 586 |
| Magnesium | | 663 |
| Sodium | | 526 |
| Aluminum | | 1,029 |
| Zinc | | 2,100 |
| Cadmium | | 15 |
| Copper | | 6 |
| Lead | | 2 |
| Manganese | | 12 |
| Titanium | | 5 |
| Phosphorus | | 3 |
| Chlorine | | 15 |
| Sulphates as ($SO_4$) | | 24,649 |
| $CO_2$ and bicarbonates as $(HCO_3)_2$ | | 2,637 |
| Silica in solution | | 17 |
| pH | 2.45 | |

[a] Bruce Williams Laboratory.

## PRELIMINARY STUDIES AND EXPERIMENTS

Experiments were conducted to determine what amounts and what compositions of mine water could be discharged into Spring River so that the mixture would not be harmful to fish life. Since the Pensacola Dam was in process of completion, particular concern was voiced by the Oklahoma Fish and Game Department over the possibility that mine-field wastes, entering the Impoundment via Spring River, might constitute the greatest single potential pollution hazard to fish and other aquatic life in the completed reservoir. While no definite allowable limits on stream pollution have ever been set for Oklahoma streams, a reasonable control was effected with the Oklahoma Fish and Game Department. Stations were set up where daily water samples could be taken and analysis made to determine the acidity caused by mineral acids and sulphates, alkalinity in ppm as $CaCO_3$, the chlorides in ppm as Cl, the sulphates in ppm as $SO_4$, and provision made to keep a close check

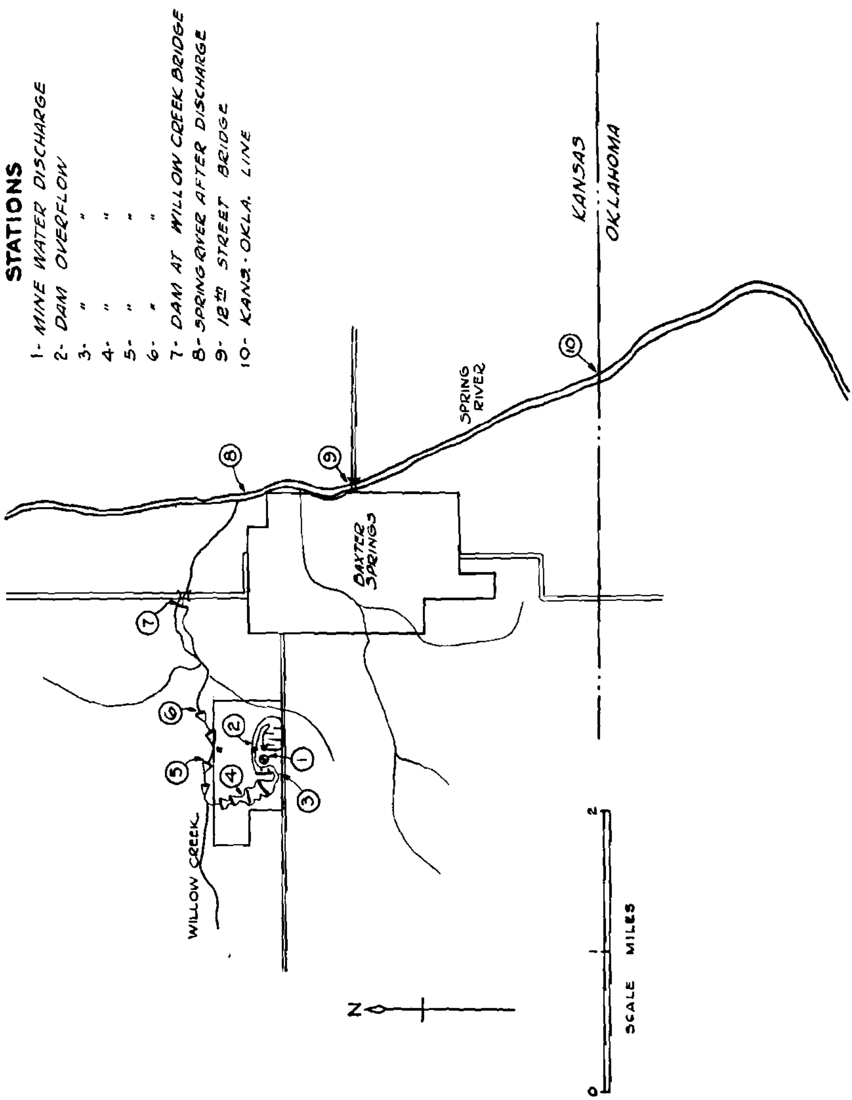

Fig 5—Plan of lime-treatment circuit with sample stations at Spring River points.

on the pH and iron content both as ferrous and ferric.

## LIME-TREATMENT CIRCUIT ESTABLISHED

Based on the results of these experiments to control the pollutant, the decision was made to design and establish a treatment circuit for the use of calcium oxide in the form of hydrated lime and an elaborate system of treatment plants and settling basins was constructed. The first function of the process was to raise the pH value, by calcium oxide treatment and aeration,

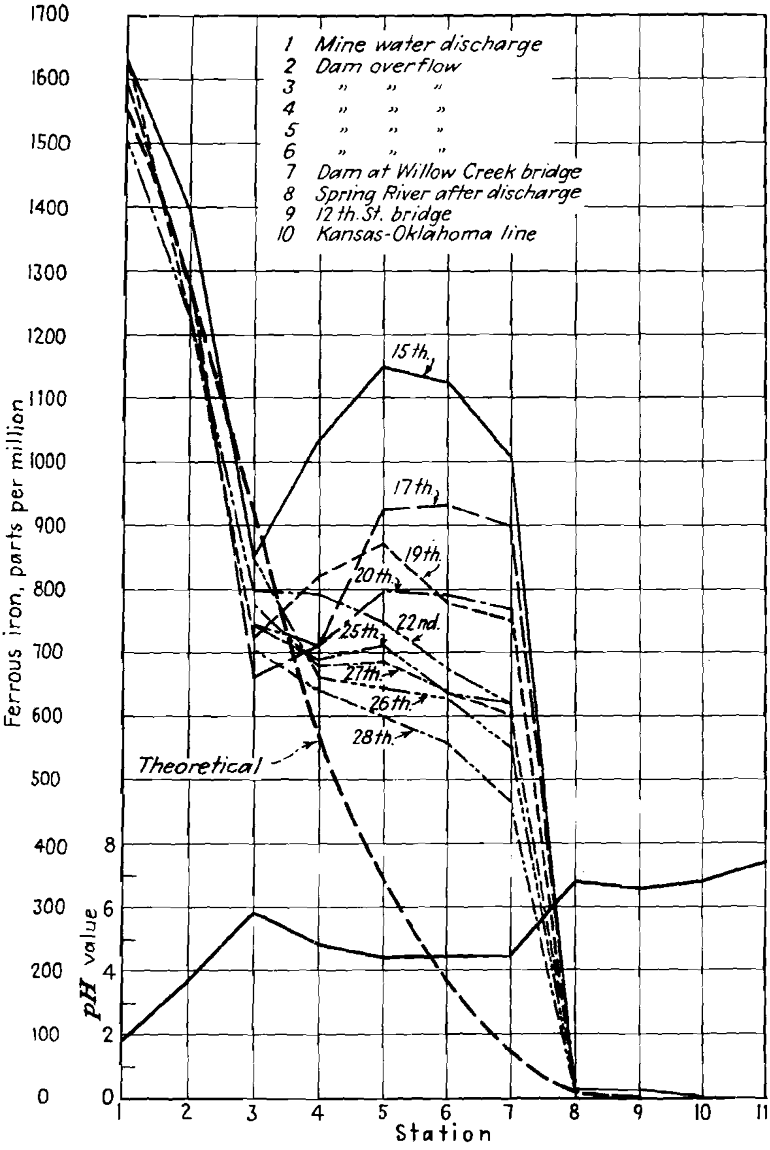

FIG 6—FERROUS IRON IN POND WATER.

to a point where precipitation of iron would take place. When the mine water was pumped to the surface it was crystal clear and was apparently saturated with iron ions and in a state of equilibrium, so that no precipitation of iron took place until sufficient oxygen had been absorbed. Considerable amounts of free carbon dioxide were also present in the water and since the iron-precipitating process involved the formation of carbon dioxide, it was necessary that provision be made for plenty of agitation and aeration to remove excessive amounts of $CO_2$. This was provided before and after treatment with hydrated lime at the various lime stations, and the settling basins were constructed of shallow depth to permit much contact with the air and to assure more thorough utilization of the lime and adequate precipitation and settling conditions. The system was also designed to take care of a maximum flow of water since it was desirous to unwater as speedily as possible, on the premise that mine-water inflows would be more neutral than the supersulphated pools.

Fig 4 shows how the circuit was designed to provide as much settling area as possible, and also shows the location of the liming and aeration stations. Fig 5 shows the same in smaller scale and locates the additional sample stations at Spring River points.

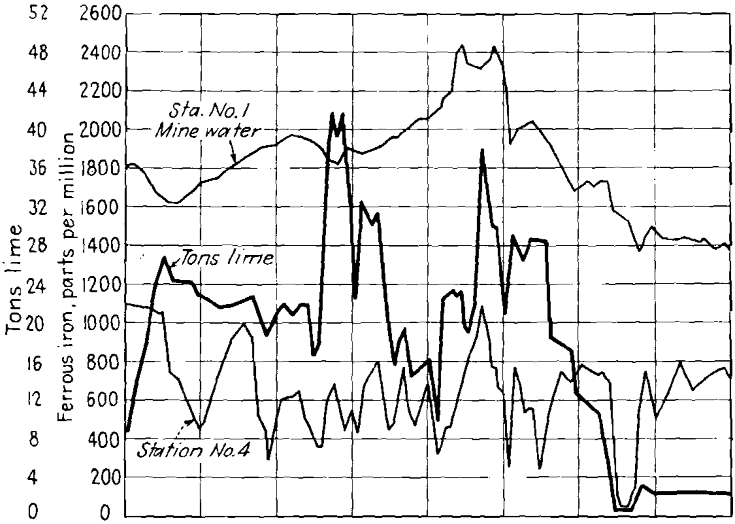

FIG 7—LIME CONSUMPTION.

Fig 6 shows graphs of the ferrous iron control when the circuit was put into operation. You will note the effect of the calcium oxide in precipitating the iron and the rise of the pH values to the point where balance was finally established. The high values following the second liming were caused by dilution of the circuit by untreated water, which occurred when a pond dam went out. This untreated water redissolved suspended iron precipitates and the full effect of the lime was not felt until the circuit was re-setablished.

## EFFECTS OF DISCHARGES INTO RIVER AND RELATIVE REACTION

You will note that discharges into Spring River carried about 500 ppm ferrous iron still in solution. Experiments had shown that at a river stage of 3 ft, the approximate flow of Spring River was 44,000 gpm and that 10 pct or about 4400 gpm of mine water running not more than 500 ppm ferrous and at a pH not lower that 4.5 would permit a dilution not injurious to fish life. The control of dilution to the limits mentioned had no effect upon the iron hydrates still left at this stage, and all the iron remaining was neutralized and precipitated at once by the excess of alkalinity and oxygen in the river and the precipitates settled out within the first mile of flow. While not injurious to fish life, this iron precipitate did prove an irritant to some landowners downstream in as much as a periodic surge of river water from a power plant upriver carried that precipitate in suspension to be redeposited in quiet water down-river where it stained shore lines with iron oxide. An additional lime station was installed in the circuit on this account and thereafter discharge in the river ran about 250 ppm ferrous.

## LIME CONSUMPTION AND FINAL DRAINAGE ANALYSIS

The lime consumption was calculated on the basis of pumping 2000 gpm of water carrying 1600 ppm ferrous. The hydrated lime used had a calcium oxide value of 74.20 pct with available hydrated lime at −200 mesh of 98.04 pct. Allowing for 10 pct aeration in the circuit the theoretical lime consumption was calculated at 23.6 tons per 24 hr. Control of the circuit was determined by accurate analysis and the lime additions varied up or down according to the amount of water pumped below or above 2000 gpm and the ferrous content below or above 1600 ppm. Fig 7 is a chart showing the amount of lime introduced into the circuit according to this plan. Cold weather had a retarding effect on precipitation as well as on the rate of settling of the precipitates and tended to increase lime consumption. In periods of heavy rain, however, lime consumption was lowered since it was possible to discharge more of the highly acid-mine water during flood periods when the ratio of stream to

TABLE 2—*Analysis of Final Drainage*[a]

| Constituents | Value | In Ppm |
|---|---|---|
| Calcium |  | 536 |
| Magnesium |  | 469 |
| Zinc |  | 585 |
| Ferrous iron |  | 2,420 |
| Ferric iron |  | 230 |
| Sodium |  | 134 |
| Aluminum |  | 287 |
| Sulphates |  | 11,005 |
| Chlorine |  | 25 |
| Hydrogen |  | 10 |
| H in terms of free $H_2SO_4$ |  | 487 |
| Carbonate alkalinity |  |  |
| Bicarbonate alkalinity |  |  |
| Silica |  |  |
| pH | 1.70 |  |

[a] Assay of mine water by Bruce Williams Laboratory.

TABLE 3—*Analysis of Neutral Mine-water Inflow*[a]

| Constituents | Value | In Ppm |
|---|---|---|
| Calcium |  | 213 |
| Magnesium |  | 80 |
| Zinc |  | 0.07 |
| Ferrous iron |  | 0.08 |
| Ferric iron |  | 0.10 |
| Sodium |  | 116 |
| Aluminum |  |  |
| Sulphates |  | 823 |
| Chlorine |  | 14 |
| Hydrogen |  |  |
| H in terms of free $H_2SO_4$ |  | none |
| Carbonate alkalinity |  | none |
| Bicarbonate alkalinity |  | 290 |
| Silica |  | 6 |
| Total dissolved solids |  | 1,542 |
| pH | 7.60 |  |

[a] Assay of mine water by Bruce Williams Laboratory.

TABLE 4—*Comparative Analysis of Spring River Water*

| Water Analysis | Spring River Above Mine Water Discharge | Spring River 1 Mile Below Oklahoma Line |
|---|---|---|
| Alkalinity, ppm as $CaCO_3$ | 107 | 74 |
| Chlorides, ppm as Cl | 9 | 11 |
| Sulphates, ppm as $SO_4$ | 58.5 | 160 |
| Non-carbonate hardness, ppm as $CaCO_3$ | 32 | 121 |
| Total hardness, as $CaCO_3$ | 139 | 195 |
| pH | 7.7 | 7.3 |

mine-water volumes was large. This was particularly true during the last stages of the unwatering. All district streams were at flood stage and we were able to complete our unwatering with large volumes even though the final mine-floor drainage of the pool carried high free sulphuric acid content, as the analysis (Table 2) shows. Pumping installations were subsequently moved to deeper level mines to the south of our property and after these were unwatered the inflow into the pool, when not contaminated by roof drips, analyzed as shown in Table 3. Finally Table 4 gives an average analysis of Spring River water before mine water was discharged *into* it as compared with a downstream analysis of the mixture below the Oklahoma line.

## CONCLUSIONS

Thus our objective, to discharge the mine water into Spring River so as to prevent undue change in the chemical quality of the river water entering Oklahoma and the Pensacola Dam Impoundment, was attained, and the unwatering of the acid-water pool accomplished.

Much has been said of the effects of acid-mine water flooding in relation to the future conservation of the Tri-State's marginal reserves. If these reserves were to be abandoned and the entire field allowed to flood, great volumes of acid water inevitably would result. When pumped in amounts necessary to again unwater the field, the neutralization and precipitation treatment of this water would assume huge proportions and entail tremendous expenditures.

However, our experiences in treating small volumes of acid water have shown that, when the neutralization costs can be borne and the necessary space for settling basins is available to accumulate the resultant hydrates, the remaining water from acid-mine drainage can be discharged into district streams without pollution.