the head tank, and the other ordinary cold water from the mains. The 1½" pipe serves to carry the hot mixture to the pot without spatter. This type has the advantage of minimum repair and mixes about 5000 lbs. of 75 per cent. acid per hour. The head tank has a capacity of 18,000 lbs. of strong acid.

The product of the plant passes through a scale tank and is delivered to the nitric acid plant where in winter weather it is mixed with 2 per cent. of nitric acid to prevent freezing. The entire product can be delivered as 99.5 per cent. H_2SO_4 , but for use in making nitric acid a portion of it is reduced to 94 per cent. H_2SO_4 .

This being a government plant the hours of labor for any one shift of men can not exceed eight. The plant is run continuously with three shifts and in addition to the men directly employed in the operation of the plant there is a superintendent who devotes about half of his time to it.

The successful operation of a contact plant, of course, depends largely upon the efficiency of the contact mass. This efficiency is easily influenced by arsenic in the raw materials. Should arseniuretted hydrogen be present in the gas entering the converter, arsenic is deposited on the platinum and is said to "poison" it. The result of "poisoning" is immediately noticeable in the temperature produced by the catalytic action and in the quantity of SO_2 unconverted. Fortunately, this effect may in part be counteracted by raising the temperature of the gases entering the converter, and for this reason hardly any two plants burning pyrites will be found using the same initial temperature. In different plants we have noted temperatures of entrance gas varying from 420° C. to 480° C. The catalytic properties of "poisoned" mass may be improved by sprinkling it with aqua regia and expelling the arsenic by the heat of the converter, or they may be entirely restored by heating the mass in a furnace after sprinkling with aqua regia.

Another factor in conversion is the quantity of SO_2 contained in the gas entering the converter. With pyrites it is customary to use an entrance gas containing not over 5.5 per cent. SO_2 with mass in good condition. When "poisoning" has occurred, this percentage must be reduced to obtain good conversion.

In this plant, using Louisiana brimstone for eighteen months, we have had no indications of "poisoning" and have not opened the converter. The temperature of gas entering the converter is kept constantly at 380° C. and conversions are regularly 95-95.5 per cent. This low temperature means a decided saving in coal, and wear and tear on the preheater. During six months the average consumption of coal has been 21.8 lbs. per 100 lbs. of SO_3 made. We believe this to be a figure decidedly less than in any Schroeder plant burning pyrites. An entrance gas of 6.5-7 per cent. SO_2 is regularly used. During six months under the above conditions, the average make has been a little more than 6 tons of acid a day, and the average yield on sulphur fed to the burner 93.36 per cent. The plant can make a maximum quantity of 8 tons with a yield of 90 per cent. Comparison of

cost sheets shows that by changing raw materials from pyrites to brimstone, we have reduced cost of manufacture nearly two dollars per ton of 98 per cent. acid; that this reduction is due in part to minimizing losses from shut-downs for repairs, in part to increased yields and in part to saving in coal and cost of upkeep.

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SMELTER SMOKE CONSERVATION.

By GEORGE C. WESTBY.

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The question of smelter smoke treatment is one of commercial metallurgy, and the application of a panacea a question of dollars and cents.

There have been many plans devised for quieting the complaints of injured agriculturists and others to whom smelter smoke seems all that is evil, but too often the proposed plan has been merely mitigatory, or has neglected provision for a material return on the investment in the plant. In other cases the process is rendered inapplicable on account of limited demand for the output whose production and sale is the vital commercial feature.

Of the methods projected for treating smelter smoke in an economic way, this article is limited to consideration of methods with which the writer has experimented.

The first of these was developed during 1902-1903 and consisted of a process for producing liquid SO_2 from the smoke, utilizing the heat of the smoke by means of economizers and air heaters. The SO_2 was to be liquefied by an ice or refrigerating machine, with the crystalhydrate of SO_2 as an intermediary product.

Aside from the mechanical difficulties incident to the arrangements for removing the flue dust, the crucial objection advanced against the process was the lack of a market for the liquid gas as produced at the rate of thousands of tons per day. The suggestion that it could be used as a refrigerant in place of ice in freight cars, and in the small ice boxes of private homes, seemed inadequate in face of the fact, that the market was both problematical and undeveloped while awaiting the expenditure of some millions of dollars in providing the necessary equipment.¹

During the course of further work in connection with the smoke problem, the idea suggested itself that the sulphurous gases of the smoke might be bound with the bases of slag and thus reduced to a more controllable form. Experiment demonstrated that the idea might be practically applied, and also suggested the general method of smoke treatment which consists in the neutralization of acid fumes on slag, and ensuing precipitation of the toxic oxides in ponds or other limited areas on the earth, chiefly as harmless and insoluble compounds with iron and other bases of the slag. As developed, the process also involved the recovery of values carried by slag and flue dust.

¹ This phase of smoke eradication method was independently educed by Dr. Carpenter, of Denver.

The fact that chilled, finely divided slag very rapidly dissolves in hot dilute solutions of HCl or H_2SO_4 , is generally known to metallurgists and chemists, and they are also acquainted with the fact that the silicic acid is retained in apparent solution. Experiment proved that hot solutions of SO_2 are also capable of effecting the dissolution of the slag in the same way; this discovery became the basis of our attack on the smoke difficulty.

In carrying out the process we have at command a hot acid smoke, laden with flue dust, vapors of sulphur and possibly arsenious or other volatilized compounds. We have also at hand granulated and chilled slag.

The acid smoke is an immediately available and intensely active chemical agent, but the granulated slag while susceptible to the vigorous attack of the sulphurous reagent, is preferably finely ground in order to accelerate its solution and incidentally reduce the size of apparatus required in its treatment. In conjunction with the smoke and slag, water or circulating ferruginous smoke liquor is necessarily used as a medium of chemical translation, in maintaining suspension of the slag pulp and in carrying the compounds formed. The slag and smoke are brought together by means of an apparatus which is introduced as a part of the flue systems. The province of the appliance is the retention of a vast surface of wetted slag in the direct path of the smoke current, in such a way that the smoke, slag dust, steam and water become as nearly as possible a hot homogeneous mist or spume.

Chemical action under such circumstances is essentially rapid, and ensures the absorption of the sulphurous gases without recourse to unwieldy apparatus or large chambers.

The result of the combination of the constituents of the mixture is the production of ferrous and ferric sulphite, ferrous sulphate, various thionates of iron and in a smaller degree sulphur salts of other bases.

The copper is mainly present in the matte particles contained in the slag, and when ground slag is used in the apparatus, remains for the most part undissolved. That portion of the copper taken in solution may be reprecipitated in the absorber by the action of polythionates developed in the smoke liquor through the interaction of the SO_2 , sulphites and free sulphur of the smoke.

In many of our experiments copper was obtained principally in an oxidized form by blowing molten slag into slag wool. In these cases the copper was maintained in solution and after discharge from the absorber was precipitated in a wooden tank by heating the solution with steam to about 80°C .

The development of thionates, on which the precipitation of part of the copper depends, requires no attention under the usual circumstances attending the roasting of ore. Their formation is encouraged in the presence of the sublimed sulphur of the smoke, and by the sulphites and the excess SO_2 of the smoke liquors. During the course of their production, there may be a constant representation of all those compounds

designated as polythionates, but the dominance of any particular form depends on the chemical and physical characteristics of the smoke, the liquor and the material treated. The thionates produced are ephemeral and finally break up into sulphates, sulphur dioxide and free sulphur as indicated in the following equation:

To illustrate a possible set of conditions occurring in the absorber during treatment of the smoke, we may take the following successive reactions:

When sodium and potassium are present in the slag they are dissolved with the other constituents and later appear as sulphates in the discharged smoke liquors, and may be recovered if desired from the residues of the evaporated liquor. Zinc if present is similarly dissolved and may be separated from other residues by volatilization or any practicable means. Lead, silver and gold are retained undissolved with the precipitated copper. In some cases green vitriol would be an important and valuable by-product.

The liquor produced in the absorption chamber may be again used or it may be continuously discharged on waste land, over which it spreads in a thin sheet that will rapidly evaporate under the influence of wind and sun. In the latter case, oxidation and hydrolysis form an insoluble basic sulphate, by translation of the green vitriol in general accordance with the equation

At the same time deposition occurs of the silicic acid and of sulphur arising from the decomposition of thionates.

Generally the liquor issuing from the absorber contains only very limited quantities of free acid. If, however, any objectionable amount of acid is present, it may be neutralized by passing the liquor over slag or through calcareous or soluble ferruginous material. In some cases the percolation of the liquor into calcareous soil would not be objectionable, as the comparatively small quantity of acid would be effectually neutralized in the formation of insoluble calcium sulphate, and thus the liquor could not seriously affect the ground water.

The flue dust carried by the smoke is effectually caught by the somewhat glutinous slag particles, and remains with the residues of the reaction chamber.

In carrying out the experiments it was recognized that the development of a simple apparatus was of the first importance; accordingly much time was spent on different tentative designs, but the aim in each case was the form of apparatus which would require the minimum of attention, repairs and adjustment.

The arrangements tried were of two general forms:

a tower or vertical chamber and a horizontal rotary apparatus.

The vertical arrangement consisted generally of a wooden tower, provided with a large number of narrow staggered shelves. These pieces were set three or four inches apart, from one end of the tower to the other. A hopper was introduced at the top of the tower for the reception of the slag and water used in the treatment. The bottom of the tower was arranged to permit the formation of a hydraulic seal at the discharge. At each end of the tower pipes were inserted; one of these was connected directly with the flue of a furnace and the other with a fan.

In operation the wet slag was charged into the hopper and was discharged from the hopper by gravity to the shelves. From the top shelves the material spread over the cross section of the tower and by the action of the series of staggered shelves, fell in splashing cascades to the bottom of the tower, coming in contact throughout its course with the hot current of acid smoke drawn through the apparatus by means of the fan.

The liquor derived by the action of the smoke on the wet slag discharged through the hydraulic seal to a large wooden tank in which the copper was precipitated by means of steam. Wooden launders conveyed the residual liquor to a pond.

The horizontal rotary apparatus was cylindrical in form. Shelves or projections were set at intervals along the interior surface, so as to lift the mixture of slag and liquor and drop it in sheets through the smoke current in the apparatus. The shelves were set at different angles so that the material would be distributed along the different planes during rotation of the cylinder. The splashing on the sides and bottom of the apparatus caused by the falling material, aided in filling the whole of the cylinder with a constant spray of absorbent mixture.

The cylinder rotated about short pipes of comparatively large diameter; these were set at the smoke entry and exit ends of the cylinder and were connected respectively with the flue of the furnace and the intake of an induction fan. The treated smoke was discharged through the fan.

Means were provided for continuously feeding the absorbent material into the cylinder, and a pump with a syphon attachment was used in removing the exhausted liquor.

The first general test was made with a rotating cylinder. The cylinder was about 10 feet in length and 30 inches in diameter.

The results of one of the experiments with the apparatus are given below:

Time.	10.15.	10.45.	11.00.	11.15.
Temp. gas inlet ° F.....	215°	220°	210°	242°
Temp. gas outlet ° F.....	82°	84°	74°	74°
Temp. water inlet ° F.....	64°	65°	65°	65°
Temp. liquor outlet ° F.....	90°	100°	78°	86°
Cu. ft. gas per min. measured at intake.....	34.2	32.4	33.0	44.4
Per cent. SO ₂ inlet.....	4.9%	4.7	5.4	4.7
Per cent. SO ₂ outlet.....	1.9	1.0	0.85	2.7
Absorption in 10 feet.....	61.2%	78.8%	84.2%	42.5%

NOTE: 140 lbs of slag charged at beginning of test; none charged during interval between 10.45-11.15.

The test gives results better than average, consequent on treatment of smaller volume of smoke per sec. than ordinary.

The test illustrates a set of experiments where the slag was not fed continuously, but was charged in one mass. The absorption in this case steadily increased for a short period after charging, then fell off rather rapidly. In the experiment given above the drop is accentuated by the increase of gas current.

In the experimental results given below the slag was practically continuously charged, although not in sufficient quantity to bring about complete absorption.

The tests were made with the tower apparatus of which the general principles have been described. Two towers were used connected at their tops. The total length of the apparatus was 77 feet. The cross section was 4 square feet.

Time.	TEMPERATURE IN DEGREES FAHRENHEIT OF				Cu. ft. gas per min.	Per cent. absorption SO ₂ by volume.
	ingoing gas.	outgoing gas.	ingoing water.	outgoing liquor.		
10.00 A.M.	320	90	96	110	68.4	81.1
10.20	355	90	..	..	84.6	79.6
10.30	355	90	..	..	84.6	82.0
11.00	355	..	..	..	84.6	82.0
1.00 P.M.	350	..	96	109	112.2	74.8
1.20	340	..	..	..	85.8	79.1
1.35	345	..	..	..	85.2	81.1
1.4	350	..	..	..	91.8	81.6
1.50	360	..	..	..	99.0	83.0
2.00	380	..	..	..	132.0	80.3
2.10	380	..	..	..	98.4	84.4
3.30	390	90	96	111	99.2	79.0

The analysis of the solutions of the set of experiments, of which the above is an example, varied with the relative quantities of slag and water charged, the rate of smoke supply, and to a large extent depended also on the temperature of the gases.

The constituents of the solutions varied between the following figures:

	MINIMUM.	MAXIMUM.
Fe.....	0.54%	3.0%
S.....	0.49%	2.9%
Cu.....	0.00%	0.8%
SiO ₂	..	3.2%

The average temperature of the incoming smoke was 393° F. and that of the discharged gases 92° F. Throughout the series the volume of smoke treated varied between 90 and 235 cu. ft. per minute.

On the whole these tests were the most satisfactory as no trouble was experienced with the apparatus or in the introduction and application of different conditions.

Succeeding the experiments described, tests were instituted for the treatment of 5000 cubic feet per minute of smoke assaying 4.5 per cent. SO₂, a volume representing the total gases discharged per minute from a 35-40 ton McDougal roaster.

The apparatus used consisted of a rotating cylinder 36 feet long and 12 feet in diameter, arranged as previously described. On account of an underestimate of the charge to be carried, the foundations, running equipment and apparatus generally were designed to sustain only a fraction of the slag and water charge necessary to absorb all of the SO₂ in the smoke;

our absorptions were therefore seldom greater than 45-55 per cent. of the SO_2 in the smoke volume. For brief periods in one case we secured absorptions of 92 per cent. and 100 per cent. We never approached a satisfactory degree of elimination of the SO_2 from the smoke, except at the expense of a breakdown with this particular apparatus. The results obtained, however, were valuable as the basis for a successful design for a cylindrical apparatus.

A study of the set of results given below will show the trend of the experiments and also make clear the limitations of the apparatus used, when it is understood that the entry "Period of run—minutes" implies "Period of anxiety before smash-up—minutes."

The entry "Slag required—theoretical" is a factor derived from the analysis of the solution, in consideration of the ratio iron dissolved to sulphur absorbed. The weight of iron dissolved is multiplied by 2.7, a constant derived from the fact that the weight of slag was approximately equivalent to 2.7 times the weight of iron contained in the slag treated.

"Slag required" represents the quantity of slag which would be required per minute, to exactly neutralize the weight of SO_2 driven from the furnace per minute. It is obvious that in practice the mere presence of this figured amount would be altogether inadequate to actually neutralize the SO_2 given off minute by minute from the furnace, since the whole of the mass is not instantaneously acted on. Depending on the degree of subdivision, the constitution of the slag and other physical and mechanical factors, a slag excess of 3,000 per cent. to 10,000 per cent. is requisite to effect a complete elimination of the SO_2 from the smoke.

	1.	2.	3.	4.	5.
Period of run—minutes...	70	57	200	280	110
Temp. of gas, entering...	250	425	400	387	250 ° F.
Temp. of gas discharge...	77	80	80	94	100 ° F.
Temp. of liquor discharge	100	118	..	130	130
Water supplied per min., lbs.	620	396	359	138	270
Total Fe in soln., lbs.	479	208	604	732	652
Total S in soln., lbs.	309	307	656	594	548
Rate of adding slag per min.	30.0	35.3	22.3	14.2	50.0
Slag required—					
theoretical per min., ...	44.3	19.4	30.8	37.8	37.0
Total available slag charged, lbs.	2120	2015	4470	3998	5512
Per cent. SO_2 absorbed of total passing through apparatus	38.2	46.8	39.0	19.8	43.3
Analysis:					
Milligrams Fe per 100 cc. solution	1008	924	1053	1897	2194
Milligrams S per 100 cc. solution	710	1360	1143	1540	1837
Milligrams Cu per 100 cc. solution	21.4	10.5	15.0	15.0	9.1

By comparison of the above data it is seen that the absorption of SO_2 tends to rise as the rate of charging slag is increased. Consideration of (2) and (5) would suggest also that the absorption rises with the temperature; this indication is confirmed in other experiments not given here. In (1) the temperature is low and the absorption high; this is probably due to the high rate of water supply combined with the comparatively high rate at which the slag wool is charged.

In order to determine the practical effect of maintaining the slag excess, which had been deduced as

the necessary amount to ensure complete absorption of all the SO_2 discharged from the furnace, during any period, we commenced a cylinder experiment by introducing before starting operation, 1500 lbs. of slag wool. The results were as follows:

PERIOD OF RUN, 10 MINUTES. 300 LBS. OF SLAG ADDED DURING RUN.

Rate of adding slag per min., lbs.	180 (comparative)
Water supplied per minute, lbs.	1195
Per cent. SO_2 absorbed	100%
Milligrams Fe in 100 cc. solution	1260
Milligrams S in 100 cc. solution	1050

After ten minutes the apparatus was stopped, measurements made and samples taken. Five minutes later the apparatus was again started and operated 15 minutes, a stop being necessary at the end of that time on account of the great weight accumulated in the apparatus—principally liquor in excess of the pump capacity.

The result at the end of the second period was:

PERIOD OF RUN, 15 MINUTES.

Rate of adding wool per min., lbs.	100
Rate of adding water per min., lbs.	1001
Per cent. SO_2 absorbed	90.2%
Milligrams Fe per 100 cc.	908
Milligrams S per 100 cc.	1036

The experiments stopped short of a commercial realization of the process, due to circumstances not affecting the question of smoke elimination. However, the net results of the work sufficiently established the following facts:

(1) The acid gases of smelter smoke can be effectively neutralized by means of chilled slag, with the complete elimination of flue dust from the discharge.

(2) The toxic action of the smelter vapors and gases can be controlled by converting them into constituents of harmless compounds and causing their deposit in an insoluble form on waste land.

(3) In bringing about the control of the gases in the manner stated, it is both feasible and desirable to recover copper, lead and other values contained in the slag and in the smoke.

(4) The conservation of by-products such as green vitriol, potash and soda salts, and silicic acid is possible where markets for the material are not too far removed from the smelting plant.

(5) The indirect use of sulphurous smoke in the treatment of wastes from the concentrator in the shape of slimes and tailings, is sometimes feasible. The reaction given below will suggest the general procedure:

$$\text{Fe}_2(\text{SO}_4)_3 + \text{SO}_2 + 2\text{H}_2\text{O} = 2\text{H}_2\text{SO}_4 + 2\text{FeSO}_4$$

$$n\text{H}_2\text{SO}_4 + \text{Cu}_2\text{S} + 2\text{Fe}_2(\text{SO}_4)_3 = 2\text{CuSO}_4 + 4\text{FeSO}_4 + \text{S} + n\text{H}_2\text{SO}_4$$

ELY, NEVADA.

NOTES ON A STUDY OF THE TEMPERATURE GRADIENTS OF SETTING PORTLAND CEMENT.¹

By ALLERTON S. CUSHMAN.

The reactions that take place when hydraulic cements are tempered with water and while the mixture is hardening are not as yet understood. It is true that many theories have been advanced in regard to the hardening process or processes but more data are

¹ Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.