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GASES VS. SOLIDS; AN INVESTIGATION OF THE INJURIOUS INGREDIENTS OF SMELTER SMOKE.

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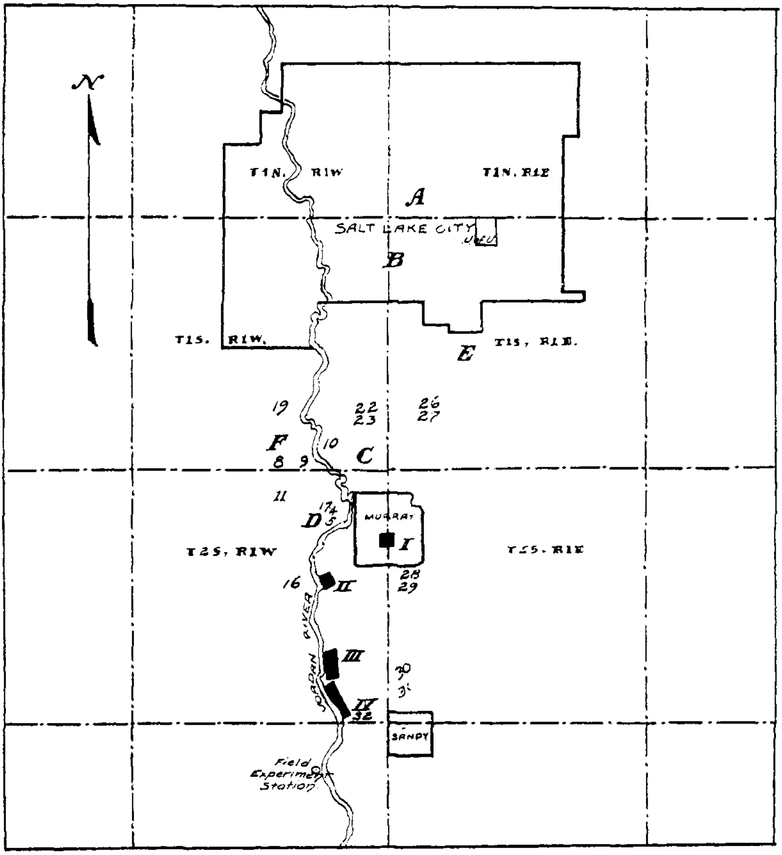
Probably the most important question confronting metallurgists and smelter men today is that of the effect of "smelter smoke" upon vegetation. During the last five or ten years there has been not only a marked increase in the number of damage suits brought against smelting companies, but, what is far more serious, suits for temporary or permanent injunctions have been begun. In some instances the latter suits have been decided in favor of the complainants. Three well known cases may be cited: (a) United States *vs.* Mountain Copper Company, whose plant is near Redding, Shasta County, California, (b) an association of about four hundred and fifty farmers in the Salt Lake valley against four smelters operating at Murray and Bingham Junction, Utah, and (c) the Deer Lodge Valley Association of farmers against the Anaconda Copper Mining Company, of Anaconda, Montana. In the first two instances judgement was rendered in favor of the complainants, and in the last mentioned the legal battle has not been concluded (January, 1907). The questions suggested by the title of this paper are of great moment in courts of law trying such cases. Moreover a complete understanding as to the relative amounts of damage caused by sulphur dioxide and solid emanations from lead and copper smelters would be of the highest value in determining the location of a smelter, the construction of its flue system and the disposition of its volatile waste products. The botanist and the practical agriculturalist are equally interested in the question.

A perusal of the literature bearing upon the smelter smoke problem shows that the view generally accepted is that the gas sulphur dioxide is responsible for the damage to vegetation, and the "fume" or finely divided solid emanation, containing arsenic, lead and copper, causes sickness and death of animals.[1] For a long time the author's view coincided with the one just given, but as the result of a large amount of experimental work carried out by him he is now persuaded that undue emphasis has been laid upon the injurious effect of sulphur dioxide upon growing field plants, and that the harmful action of the solid emanations from the smelters, the so-called "flue dust," has been seriously underestimated.

Several facts should be noticed in connection with the damage sustained

FIG. I.

Map showing locations of (a) Smelters, (b) Aspirator Stations, (c) Field Experiment Station, (d) places where samples were collected.



Legend: I. Murray Plant of American Smelting and Refining Co. Lead Smelter.
II. Copper Smelter of Utah Consolidated Mining Co., Highland bog Plant.
III. Copper Smelter of Bingham Consolidated Mining and Smelting Co.
IV. Copper and Lead Smelters of United States Mining Company. A, B, C, D, E, F—Aspirator Stations.

[1] Haselhoff and Lindau "Rauchbeschädigung." Gebrüder Bornträger, Leipzig. Haywood, "Injury to Vegetation by Smelter Fumes," Bull. 89, Bureau of Chemistry, U. S. Dept. of Agriculture.

by vegetation in the Salt Lake valley. In the first place the injury does not occur simultaneously over a large area; on the contrary it seems to be restricted in its range. Secondly, it is rarely found that a number of crops grown successively in a given locality show the effect of smoke. Finally, the blighting action of the smoke is observed at its maximum during wet weather and at its minimum when the atmosphere is dry. The result is that one seldom finds a farmer complaining about a total loss of crops, and it is this element of partial loss, varying from year to year, that makes the legal question of damages hard to decide.

Thinking that it might be of interest to know the average amount of sulphur dioxide in the atmosphere of this section of the country, a series of experiments was carried out by the author in the early part of 1905. A number of students from the Department of Chemistry consented to act as observers and were placed in charge of stations distributed over the northern part of the valley. No students from the section of the country lying south, east and west of the smelters went to and from their homes daily, consequently no stations could be established there, desirable though they would have been. The situation of the smelters, stations and other points to be referred to later can be learned from the accompanying map (Figure 1).

Each station was provided with an aspirator and absorption bottle. Known volumes of air, approximately twenty liters each, were drawn through solutions of iodine, and later these solutions were analyzed for their sulphuric acid content by the ordinary gravimetric method. An approximate calculation as to the amount of sulphur dioxide by volume in a million parts of air could then be made. A summary of the results is shown in Table 1. It may be said that a second series of determinations carried out in the autumn of 1905 corroborated the results here given, although carboys were used as aspirators, two absorption bottles in train were employed, and forty liter samples of air were analyzed.

TABLE I.

Summary of results of analyses made to determine the average sulphur dioxide content of the atmosphere in the Salt Lake Valley.

Parts SO_2 Per million.		Stations A	B	C	D	E	F	Total	Per cent. of Total
0	Number of Analyses	89	38	98	53	28	5	311	59.35
1		20	12	10	13	2	3	60	11.45
2-3		32	11	32	16	12	2	105	20.04
4-6		10	3	14	6	1		34	6.50
7-10		1	1	3	3		2	10	1.91
Over 10				4				4	0.76
Total		152	65	161	91	43	12	524	

So far as the practical value of these results is concerned it must be admitted that they do not carry much weight. Air charged with enough sulphur dioxide to do damage to plants might be present for ten, twenty or thirty minutes, but when this quantity is averaged over a twelve or twenty-four hour period it makes the result appear so insignificantly small as to be almost negligible. Nevertheless the very small amount of sulphur dioxide found is certainly surprising.

It would be very desirable to have a method of analysis that would enable one to determine with accuracy the amount of sulphur dioxide in the atmosphere at a given time and and place, not an average over a long period, but such a method is unknown to the author.

A rough estimate as to an upper limit of the sulphur dioxide content of the air at a given distance from the smelter can be made if (a) the size of the stacks, (b) sulphur dioxide content of the stack gases, (c) width and thickness of the visible smoke column at a given time and place, be known. Measurement of the combined smoke columns coming from a group of smelters at a distance of a mile from the nearest one, showed the width to vary from one to three thousand feet according to the atmospheric conditions. Granting that the sulphur dioxide did not exceed one and a half per cent by volume in the gases as they issued from the stacks, that the smoke column became at least one third as thick as it was broad, and that the combined areas of the stacks in question was known, it could be shown by proportion that the possible sulphur dioxide content would not exceed one part in forty or fifty thousand at the place mentioned. Diffusion, however, would surely tend to make the possible content still lower.[1]

Probably the best summary of the effects of sulphur oxides upon plants is that given by Haselhoff and Lindau.[2] The authors are well known botanists and chemists, and their compilation of the work of others and their original contributions to the knowledge of the subject in hand show characteristic German thoroughness. In effect they say:

"1. Even after severe and oft-repeated action upon the soil of the sulphurous and sulphuric acid contained in smoke, whether the action be direct or by means of atmospheric precipitation, an essential increase in the sulphuric acid content of the ground does not take place. Apart from a transposition of the constituents of the soil no change in its composition occurs, and therefore one can scarcely tell whether an injury to the soil has been caused by the sulphurous and sulphuric acid gases in the smoke.

"2. The direct action of free (uncombined) sulphurous or sulphuric

[1] Analyses made by the writer have shown that the sulphur dioxide content of the gases in the various lead stacks varies from 0.20 to 0.50% by volume, gases in copper stacks (blast furnace and roaster) from 0.90 to 2.50 %, and gases in converter stacks from 0.20 to 1.20 %. In reverberatory stacks the quantity of sulphur dioxide is negligibly small—0.01 % or less.

[2] Loc. cit., pp. 143-145.

acid of smoke upon the roots of plants is improbable under the ordinary conditions of agriculture and forestry. Should an increase in the sulphate content of the soil take place, through the action of the sulphurous and sulphuric acid gases in the smoke, it is without influence upon the growth of plants; therefore an injury to vegetation by acid smoke gases acting by means of the soil is as good as excluded.

"3. An injurious effect from acid smoke gases acting upon plants can only take place if the said gases come directly in contact with the leaf organs of the plant.

With damage to vegetation by these acids there always goes parallel increase in the sulphuric acid content. The latter shows itself also in uninjured plants grown upon a soil rich in sulphates, and therefore a high sulphate content cannot always be accepted as proof of damage by smoke. Far more important in this connection are the conditions of the locality in which the plants were grown.

"4. The sensitiveness of plants toward sulphuric and sulphurous acid varies; even plants of the same kind are more or less sensitive according to their individual idiosyncrasies.

"5. The long continued action of sulphurous acid, even in quantities as small as one part per million, has proved hurtful to plant growth. According to the experiments of M. Freytag sulphuric acid proved to be the more injurious, and according to the experiments of J. von Schroeder, less injurious, than sulphurous acid.

"6. The masses of sulphurous acid taken up by equal leaf surfaces of two different plants under like conditions and in the same time, do not give a measure of the damage which the plants have suffered; on the contrary the specific peculiarities in the make-up of the individual plants must be taken into account.

"7. Fissure openings of the leaf organs play no role in the absorption of sulphurous acid; the gas is taken up principally by the whole leaf surface, and not by fissures. Therefore the difference in the amounts of sulphurous acid that penetrates into the leaf is not to be explained by the number of fissures, but by other conditions dependent upon the organization of the individual plants.

"8. The effect of sulphurous acid is to cause a derangement of the water circulation, which is made manifest by an increased loss of water and leads to the drying out of the leaves.

"9. The absorption of sulphurous acid,—and accordingly the destruction of the water circulation,—is greater for a given quantity of sulphurous acid in the same time in the presence of light, at a high temperature and in dry air, than in the dark, at a lower temperature and in damp air; consequently sulphurous acid and the acid smoke gases are generally more injurious by day than by night.

"10. Morphologically the effect of sulphurous acid shows itself in the formation of spots on leaves, the dying off of leaves and twigs, the "falling behind" of the yearly growth in thickness, and finally the death of the plant.

"11. In the interior of the plant cells plasmolysis is developed, the chlorophyl grains die and finally form with the plasma and the other contents a brown amorphous mass. At the same time the tannin usually separates, especially where the injury has come about gradually, and can be recognized by the brown or black nuclei ("Zusammenballungen") in the cells.

"12. We have represented the sulphurous acid as destroying the life of the plasma in the cell. Probably it acts as sulphuric acid, which is formed by the oxidation of the sulphurous acid with the oxygen of the assimilating chlorophyl grains, in the presence of water derived from the cell sap.

"13. By the continuous action of water, as for example rain, the absorbed sulphurous or sulphuric acid in the dead leaf organ can be separated again. In the case of conifers, and probably also in other plants whose leaves are resinous or waxy, the sulphurous or sulphuric acid content, absorbed from the smoke gases, is not washed out again by the rain, and the recognition of smoke injury by this means is not possible.

"14. There is not known an absolutely certain botanical means of recognizing damage caused by sulphurous acid, but it is only possible to determine its presence through the combined evidence of the external and internal injuries. The surest proof is the chemical analysis for sulphuric acid."

Concerning paragraph 5 it should be noted that in the open country one seldom finds sulphur dioxide acting for a long continued time in one place. Ordinarily the smoke is blown about by the wind, thus making its action upon plants at a given place intermittent. During periods when the smoke is not present the plants show a tendency to recover.

The statements of paragraphs 3, 8, 9, 13 and 14 should be borne in mind when one compares the work of chemists who have experimented with pines, firs and other conifers, with that of chemists who have studied injuries caused by sulphur dioxide acting upon lucerne, sugar beets, beans, peas and other plants with soft succulent leaves.

Most of the experiments with plants thus far reported have been carried out with potted specimens or with such as grew in greenhouses. Of course under these more or less artificial conditions one might expect to obtain results somewhat different from those given

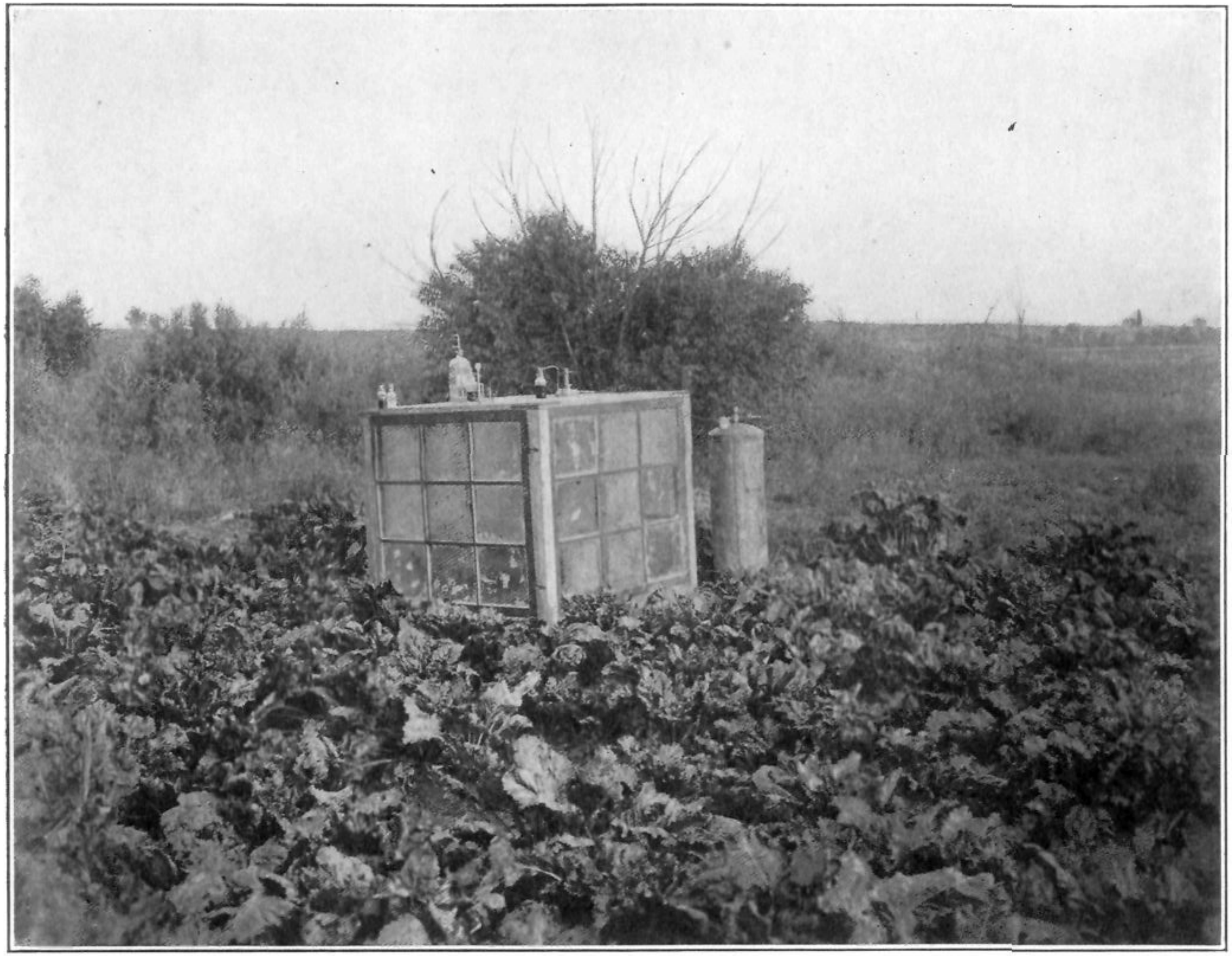


FIGURE 2.
Cabinet for Use in Fumigation Experiment.

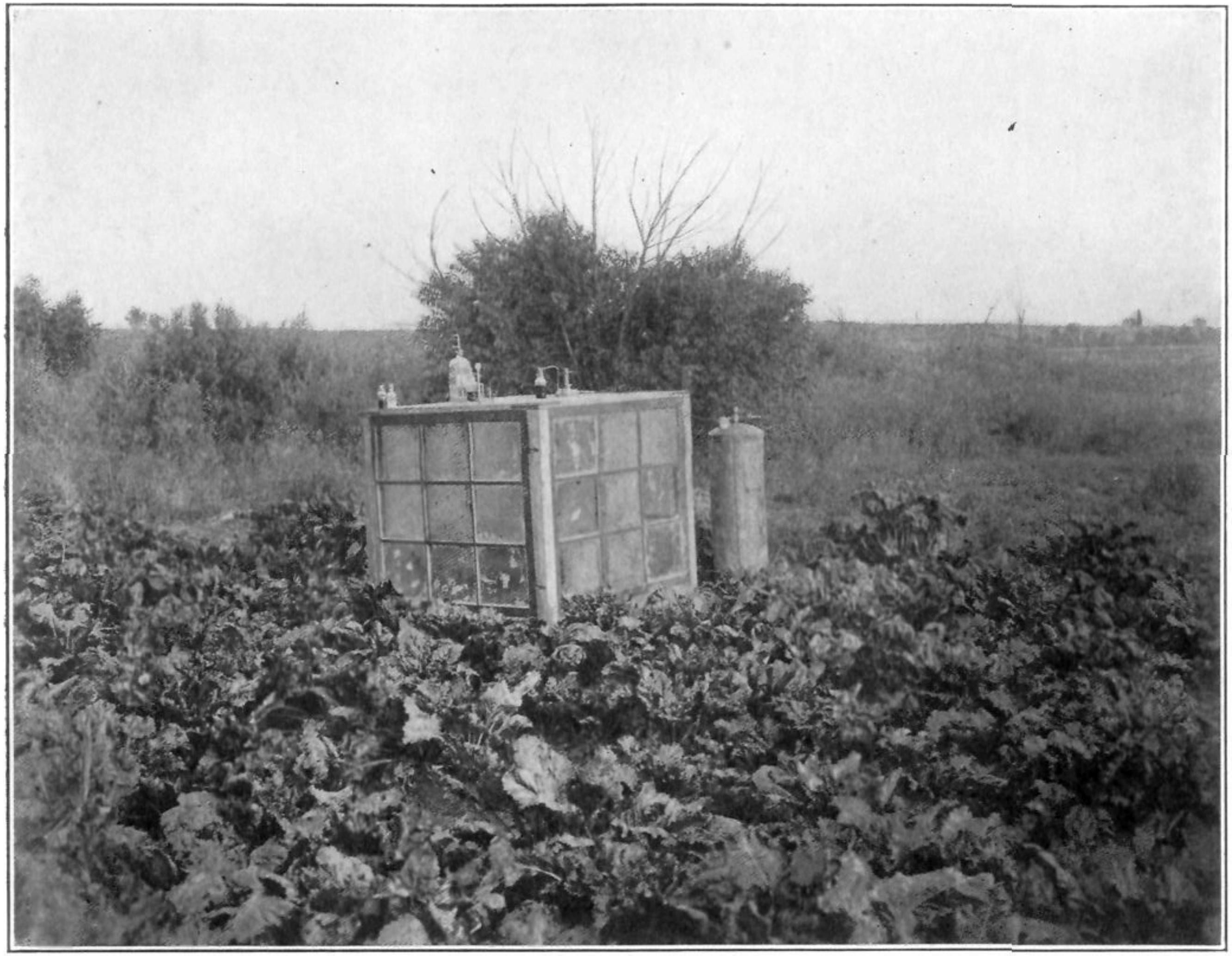


FIGURE 2.
Cabinet for Use in Fumigation Experiment.

by field plants growing in place, consequently in all our experiments we used only field plants.

A sectional cabinet was built so as to be transported readily. (Fig. 2). Through the top were suspended several thermometers, a fan for causing a mixture of the gases, and an inlet tube for the sulphur dioxide. This inlet tube consisted of one leg of a tube provided with a two-way stop-cock, another branch of which led through a bottle containing a known amount of iodine solution. When ready for an experiment the plants surrounding those selected for the trial were cut away, and the ground was loosened up in order to let a square frame rest securely upon it. The cabinet was then placed upon the frame, the door shut, and earth piled about the base. The dimensions of the cabinet (four feet on a side) and the temperature and pressure of the atmosphere being known, it was possible to calculate how much sulphur dioxide, by volume, would be required to give in the cabinet a mixture of gases containing a known quantity of this active constituent. A definite amount of standard iodine solution, equivalent to a known volume of sulphur dioxide, was placed in the absorption bottle, a steady stream of sulphur dioxide admitted to it through one leg of the two-way tube, and the time required for decolorization of the iodine and starch carefully noted. At the end of the operation the stop-cock was quickly reversed and sulphur dioxide admitted to the cabinet long enough to give in it a mixture of the required concentration. As a check upon the accuracy of the first measurements and upon the steadiness of the gas current, a second known quantity of iodine was placed in the absorption bottle and the current of gas diverted to it at the conclusion of the "charging" of the cabinet, and the time required for decolorization again noted. The pressure of the gas in the tank being rather high and the amount of sulphur dioxide used in an experiment being rather small, it was believed that the current would be steady during the time of charging, that the measurements would be accurate to within at least ten per cent. and that the results would be preferable to those obtained when a sulphur-bearing compound was burned in a cabinet to generate a known amount of sulphur dioxide. With the aid of this cabinet, experiments were carried out upon sugar beets and alfalfa growing in a certain field about one and a half miles south of Bingham Junction, Utah. The dilute sulphur dioxide was allowed to remain in contact with the plants one hour and was then removed by opening the door and permitting fresh air to enter. After a known interval the process was repeated. Six or seven fumigations daily were carried out, the cabinet being allowed to remain open at least an hour between treatments and from 8.00 P. M. until 7.00 A. M. in cases where the experiment required more than six or seven fumigations.

In the case of lucerne (alfalfa) two treatments with sulphur dioxide equivalent to one part in ten thousand caused a slight wilting. Three more treatments caused incipient bleaching as well as withering. At the end of the seventh treatment the plants were quite bleached.

Four treatments with sulphur dioxide equivalent to one part of the gas in twenty thousand of air caused wilting, but no bleaching. Incipient bleaching was noted after the fifth treatment, and after the seventh fumigation the plants were decidedly bleached and withered.

Eight treatments with sulphur dioxide equivalent to one part of the gas to fifty thousand of air caused wilting, but practically no bleaching. After the ninth treatment bleaching was observed, and continued to become worse with succeeding fumigations. Even after twelve treatments the lucerne did not look so badly as did that which had been treated with a more concentrated sulphur dioxide only half that number of times. A series of experiments run as a "dummy" or blank, in which all the operations were carried out for a whole day just as in regular determinations, except that no sulphur dioxide was used, resulted in no evident injury to the plants treated.

In the case of sugar beets two treatments with one part of sulphur dioxide to ten thousand of air caused very evident wilting, accompanied by blackening. Bleaching began with the third treatment and increased to the fifth, when the plants were thoroughly ruined so far as their foliage was concerned.

Analogous results were obtained with sulphur dioxide one half as strong as the above, and the operation was discontinued after the seventh fumigation.

Twelve treatments with one part of sulphur dioxide to fifty thousand parts of air produced no visible injury. The same plants were then treated with one part of sulphur dioxide to thirty-three thousand parts of air, and after three more treatments slight wilting was evident. Fumigations were then stopped, but several days later these wilted spots, under the influence of the sunlight, presented a marked bleached effect.

Thus it will be seen that sulphur dioxide, when diluted to the amounts that can be present in the air of a smelting district, must be applied repeatedly to plants in order to cause material injury. Contrary to the statement of Haselhoff and Lindau (paragraph 9 above) observations of field conditions in this vicinity seem to show that damage is rare during bright, clear dry weather, but usually occurs during damp, "heavy" weather. With this fact in mind our fumigations were carried out in the presence of sufficient moisture to simulate these worst conditions, and we have every reason to believe that had less moisture been present in the cabinet the injury shown would have been less in amount. The temperature range during the experiments was normal for the time of year (August and September).

A series of experiments with sulphur dioxide in aqueous solution, sprayed and poured upon alfalfa and sugar beets, was carried out. Solutions containing 2.91, 2.33, 1.75 and 1.46 grams of sulphur dioxide per liter when *sprayed* upon beet plants, using an atomizer, produced but slight effects, simply a few spots of yellow to white corrosion here and there. The same strengths of solutions when *poured* upon beets caused considerable corrosion. The latter statement applies also to solutions containing 1.17 to 0.87 grams of sulphur dioxide per liter when poured upon the beets. Weaker solutions than the above, whether sprayed or poured, produced little, if any injury. (See Table 2). In each experiment the leaves were treated with the reagent once only.

Analogous statements can be made concerning lucerne, but the action is far less marked.

As a corollary it might be said that solutions of sulphuric acid in quantities equivalent to the sulphur dioxide mentioned above, if present to the extent of 1.38 grams per liter or stronger, produced marked corrosion, whether sprayed or poured upon the plants. More dilute solutions (0.46 grams per liter or less) when used upon beets caused but little, if any, damage. (See Table 3.) Lucerne seems to possess slightly greater power of resistance to sulphuric acid than does the sugar beet.

For several reasons the question of the solubility of sulphur dioxide in water has a peculiar interest. By some the suggestion has been made that this gas be removed from the smoke by means of a suitable scrubber. By others it has been claimed that the fog and rain dissolve large quantities of sulphur dioxide and thus cause great damage to substances with which they come in contact. A few considerations concerning the possible strengths of solutions that could be formed from the gas in smelter smoke may not be out of place.

According to Schönfeld[1] pure sulphur dioxide, if allowed to remain in contact with water, will be dissolved or absorbed to the following extents at the temperatures stated:

Temperature.	Pressure.	Volume of Sulphur Dioxide per Volume of Water.
32° F	760 mm.	79.8
41	"	67.5
50	"	56.6
59	"	47.3
68	"	39.4
77	"	32.8
104	"	18.8

Applying the well known law of partial pressures of gases to such gas mixtures as escape from smelter stacks at this altitude, we find that the

[1] Ann., **95**, 5.

TABLE 2.

Experiments to Determine the Effect of Aqueous Solutions of Sulphur Dioxide upon Sugar Beets.

Plant Number.	Treatment.		Result on Leaf.	Beet Measurements. Length	Circumference.	Weight.	Polariscope.	Condition at time of analysis.
255	SO_2 2.91 g/l	Sprayed	Corroded in a few small spots.	See Table No. 14.				
256	" "	Poured	More corroded than 255.	9 in.	9 in.	13.5 oz.	15.2	Soft.
257	" 2.33 g/l	S	Corroded in a few small spots.	See Table No. 14.				
258	" "	P	Much corroded over large areas.	9	14	35.5	13.0	Hard.
259	" 1.75	S	Corroded in a few small spots.	8	10	13.5	15.6	Rotten half way up core.
260	" "	P	More corroded than 255.	9	10.75	18.5	14	Soft.
261	" 1.46 g/l	S	Corroded in a few small spots.	12	14	39	13.4	Hard.
262	" "	P	More corroded than 255.	10	9	10.5	18.6	Rotten places at core.
263	" 1.17	S	Little injury, if any.	12	12	26.5	17.0	Soft.
264	" "	P	More corroded than 255.	7	8	7	20.0	Soft.
265	" 0.87	S	Little injury, if any.	7.5	9.5	9.5	18.6	Soft.
266	" "	P	More corroded than 255.	9	11	18	12.8	Soft.
267	" 0.58	S	Little injury, if any.	10.5	13.75	34	13.8	Hard.
268	" "	P	" "	14	14.5	41	16.8	
269	" 0.29	S	" "	11	10.75	23.75	14.8	Hard.
270	" "	P	Some white spots.	9	12	24.5	14.2	Hard.
271	" 0.15	S	Ditto No. 263	10.25	17	35.5	14	Hard.
272	" "	P	" 263	11	14.5	42	15.8	Hard.
273	" 0.06	S	" 263	11	11.5	24.5	17.2	Hard.
274	" "	P	" 263	13	11	26	16.4	Hard.
275	" 0.03	S	" 263	7.5	9	9.5	18.0	Hard.
276	" "	P	" 262	10.5	13	28	15.8	Soft.

following volumes of sulphur dioxide could be absorbed by one volume of water:

Average Sulphur Dioxide by Volume.		Min. 0.75%	Max. 3.00%
Temperature.	Pressure.	Volume of Sulphur Dioxide per Volume of Water.	
32° F	650 mm.	0.56	2.04
41	"	0.43	1.70
50	"	0.36	1.42
59	"	0.30	1.20
68	"	0.25	1.00
77	"	0.21	0.83
104	"	0.12	0.48

Attempts to prepare a saturated solution of sulphur dioxide from the flue gases of a certain smelter in August, 1906, resulted in solutions that contained as a maximum 0.33 volumes of sulphur dioxide per volume of water. As the temperature at the time of the experiment varied from 95 to 102° F. and the sulphur dioxide content of the gas from 1.3 to 1.5 per cent., the concordance of the theoretical and the actual values is sufficiently close for all practical purposes. To an atmosphere containing less than the indicated percentages of sulphur dioxide, under the given conditions of temperature and pressure, the said solutions would give up some of their sulphur dioxide and thus become weaker. These conditions would obtain as soon as the gases had escaped from the stack and had a chance to diffuse.

The possibility of dissolving sulphur dioxide from the smoke and thus eliminating the "smoke nuisance" is thus seen to be very slight indeed, especially in a semi-arid district where water is valuable. And granting that the gas could be so dissolved, what disposition could be made of the product?

Directing attention to the injury caused to plants by "flue dust" we must state at the outset that by this term we mean *not* the gross heavy material that settles in the flues near the furnaces, roasters or reverberatories, but the finely divided substance that finds its way to the stack and even out of the stack. The term "solid emanation" would probably be a better name than "flue dust." It was noticed some time ago that a cold body, such as a tube cooled by a current of air, held into a stack condensed upon its surface a deposit of solid matter. This solid matter resembles that which is found at the terminus of a long flue system or at the top of a stack. The analogy in composition is shown by Table 4. Dust No. 3 consisted of a concretion and mass of dust broken from the top of a stack; Dust No. 4 was taken from flues near the roasters, and Dust No. 8 from a flue leading from copper blast furnaces, but not at the base of the stack. The results obtained from these three samples are scarcely comparable with those obtained from the six others, which were either collected at the end of a long flue system or by condensation upon tubes, as referred to above.

TABLE 3.

Experiments to Determine the Effect of Dilute Solutions of Sulphuric Acid upon Sugar Beets.

Plant Number	Treatment.		Result on Leaf.	Length	Circumference.	Weight.	Polariscope	Condition at time analysis
277	H_2SO_4 4.6g/l	Sprayed.	Badly corroded, small white and brown spots.	13	18.25	73 oz.	13.2	Hard
78	"	Poured.	Badly corroded, over large areas.	12	14.5	38	13.2	Soft
79	" 2.76	S	Ditto No. 277	See Table No. 14.				
80	"	P	" 278	13.5	9.5	23	17.8	Soft
81	" 1.38	S	" 277	10	12.5	33	16.8	Soft
82	"	P	" 277	10.5	10	16	20.2	Soft
83	" 0.46	S	Little injury, if any	9.5	12.25	24	18.0	Soft
84	" "	P	" "	14	13	40	13.6	
85	" 0.23	S	" "	10	12	28	14.6	Hard
86	" 0.23	P	" "	13	14	36	16.8	Hard
87	" 0.09	S	" "	11.5	15	45.5	15.4	Hard
88	" "	P	" "	9	15.5	32	18.8	Hard
89	" 0.05	S	" "	11	11	32.5	16.0	Soft
90	" "	P	" "	9	12	27	18.4	Hard

TABLE NO. 4

Analyses of Flue Dust

	Moisture Per cent.	Water Sol. "SO_3" Per cent.	Total "SO_3" Per cent.	Water Sol. Fe Per cent.	Total Fe Per cent.	Water Sol. Cu Per cent.	Total Cu Per cent.	SiO_2 Insol. Per cent.	Pb Per cent.	As. Per cent.	Zinc Per cent.
Flue Dust 1....	2.0	15.7	26.8	3.3	15.2	1.6	5.1	21.6	6.0	9.75	0.65
" " 2....	0.7	14.2	27.3	3.6	18.3	0.5	3.5	22.9	10.7	6.14	.95
" " 3....	4.1	17.7	33.9	3.6	16.7	1.6	4.2	28.5	0.8	.83	.15
" " 4....	0.1	6.7	20.6	0.2	8.1	Trace	2.2	31.4	16.3	1.31	4.40
" " 5....	0.3	6.1	21.0	0.8	10.3	Free	1.0	18.0	19.7	13.52	4.25
" " 6....	0.9	6.9	24.4	0.7	9.4	"	0.3	16.6	24.1	10.26	1.25
" " 7....	3.3	17.8	29.0	4.2	9.6	0.8	1.5	15.8	15.5	6.00	1.90
" " 8....	0.7	2.3	31.8	0.0	33.0	Free	3.7	27.4	2.4	.47	.95
" " 9....	not analyzed.										

It has been suggested that the corrosive power of the dust is due to the presence of sulphur trioxide closely associated with the solid particles, but not necessarily in combination with them. In the roasting process conditions are especially favorable for the production of sulphates, which afterward break up into metallic oxides and sulphur trioxide. Moreover the metallic oxides formed from the burning of sulphides are recognized as good catalyzers, and in their presence it is not improbable that some of the sulphur dioxide at first produced may unite with the excess of oxygen necessarily present. To test the hygroscopic power—which may be accepted as an indication of the sulphur trioxide content—of the dusts used in these tests, weighed samples were placed on watch glasses and supported over water, but protected from the outer air by improvised bell jars. At intervals the powders were weighed, and after the lapse of two hundred hours were dried to constant weight at 105°. The following table gives the per cent. of moisture originally present and the moisture content after twelve, twenty-four and forty-eight hours:

TABLE NO. 5.

	Moisture Content Originally. Per cent.	Moisture Content after Twelve Hours. Per cent.	Moisture Content after Twenty-four hours. Per cent.	Moisture Content after Forty-eight hours. Per cent.
Dust No. 1	2.04	16.22	21.83	23.36
" 2	1.76	10.17	14.40	16.59
" 3	4.23	10.21	12.05	13.09
" 4	0.09	3.39	5.20	5.60
" 5	0.35	3.01	5.87	6.87
" 6	0.91	2.98	4.19	4.44
" 7	3.43	5.80	9.88	11.48
" 8	0.69	1.56	2.78	1.67

With the exceptions of Dusts No. 5 and No. 6 it was found that the corrosive power was roughly proportional to the hygroscopic power, but that in these two instances, although the corrosive power was great, the hygroscopicity was low. Could their corrosiveness be due to their high arsenic content?

Unlike stack gases, which are diluted and carried great distances,—upward, as well as in other directions—by the process of diffussion, solid emanations are bound to settle. For them there is no fortunate diffusive action. By the use of dust collectors one can gather samples of this material even at considerable distances from a smelter. Near a smelter unprovided with good dust- or fume-arresting devices one can even find particles of appreciable size settling upon the clothing, and if these little particles be touched with the tongue their acrid, burning property is made manifest. The analyses of hay gathered from stacks and sheds (Table 6), dust collected from rafters in protected places (Table 7), soil from particular localities (Table 8), and the viscera of animals said

TABLE NO. 6.

Partial Analyses of Lucerne Collected in the Smelter Zone.

		Pb.	Cu Per cent.	As. Per cent.
Sample No. 4	Lucerne	Absent	0.0024	Trace
" 11	"	Absent	.0012	Trace
" 17	"	Trace	Trace	0.001
" 19	"	Trace	0.002	0.001
" 30	"	Trace	0.006	Trace
" 31	"	Absent	0.006	Absent

to have been poisoned by pasturing in parts of the "smoke zone," show that some of the solids thrown out from the stacks find their way considerable distances, the maximum amount, of course, being distributed in the directions of the prevailing winds. The quantity of solids thrown out by a given smelter naturally depends upon the nature of the ore used, the metallurgical processes employed, the extent and kind of fume-arresting devices installed, and possibly upon other factors.

TABLE NO. 7.

Partial Analyses of Dust Gathered from Rafters in Barns, Sheds, etc.

			Pb. Per cent.	Cu. Per cent.	As. Per cent.
Sample No.	5	Dust from Rafters in Shed	Trace	0.912	Trace
"	8	" " "	Absent	0.057	Trace
"	9	" " "	Trace	0.337	Trace
"	10	" " "	Trace	0.255	Trace
"	16	" Gutter around house	0.185	0.160	0.051
"	23	Dust from Rafters in Shed	0.069	0.024	0.003
"	24	" " "	Trace	0.088	0.009
"	27	" " "	0.338	0.235	0.121
"	29	" " "	Trace	0.036	0.006
"	32	" " "	0.124	0.167	0.049

[1] Lead and arsenic not determined quantitatively.

TABLE NO. 8.

Partial Analysis of Soils.

		Pb. Per cent.	Cu. Per cent.	As. Per cent.
Sample No. 22	Soil	Trace	0.018%	0.004%
" " 21	"	Absent	Absent	Trace

Several series of experiments with "dust" upon sugar beets and alfalfa were carried out. In Series No. 1 the dust was treated with water, solutions representing 3, 2, 1 and 0.5 per cent. of the solid being made. These solutions were sprayed upon plants and the result in general was very severe corrosion. One treatment was given to each plant. As was to be expected Dusts No. 4 and No. 8 were scarcely injurious at all, and Dust No. 3 occupied an intermediate position in this respect between the coarse materials (No. 4 and No. 8) on the one side and the fine dust (No.'s 1, 2, 5, 6, 7 and 9) on the other. (Table 9).

In Series No. 2 Dust No. 2 was mixed with soil in varying quantities at dusted upon the plants. A mixture of the dust with nine times its weight of soil produced practically no effect upon the plant, but in cases where the dust made up twenty per cent. or more of the mixture the results upon the plants were literally "frightful." It would seem that the corrosive power of the solid emanation is neutralized in whole or in part by mixing it with a sufficient quantity of soil. (Table 10).

TABLE 10.

Experiments to Determine the Effect of Mixtures of Flue Dust and Soil upon Sugar Beets.

Plant Number.		Treatment.	Result on Leaf.	Length.	Circumference.	Weight	Polariscope.	Condition at time of analysis.
213	100%	Flue Dust No. 2	Ditto 201. All leaves	11	16	58	14.8	Soft
214	50	" "	frightfully corroded	9.5	13.75	27.5	19.6	Hard
215	20	" "	" "	10.5	13.0	23.5	17.0	
216	10	" "	Corroded but little	10	11.75	21.75	19.0	
217	5	" "	Little injury, if any	See Table No. 14.				
218	3	" "	" "	7	10	13.5	18.8	Hard
219	2	" "	" "	7.5	10.5	14.25	16.4	Hard
220	1	" "	" "	See Table No. 14.				
221	0.5	" "	" "	7	9.25	9.5	21.8	

TABLE 9.

Experiments to Determine the Effect of Aqueous Solutions of Flue-Dust upon Sugar Beets.

Plant number		Treatment	Result on Leaf	Length	Circumference	Weight oz.	Polariscope	Condition at time of Analysis
201	3%	Solution	Very badly corroded	13in	14 in.	41.5	12.4	Hard
202	2	Flue	" " "	13.5	13	32	12.4	Hard
203	1	Dust	" " "	12	13	31.5	17.4	Soft
204	0.5	No. 1	" " " not so extensive	12	16	45	13.4	Hard
205	3%	Solution	" " "	12	12	22.5	13.8	Hard
206	2	Flue	" " "	8	9.5	13.0	14.8	Hard
207	1	Dust	" " "	11	16	43	15.6	Hard
208	0.5	No. 9	" " "	12.5	13.5	38	18.8	Hard
209	3%	Solution	Ditto No. 201	11.0	14.5	36	12.6	Hard
210	2	Flue	Ditto No. 204	14.0	15.0	44	17.6	Hard
211	1	Dust	"	9	10.25	15	19.6	
212	0.5	No. 2	"	10.5	13	34.5	13.6	Soft
222	3%	Solution	Corroded in spots	13	14.0	45.0	15.6	
223	2	Flue	" but not so marked. See table No. 14					
224	1	Dust	" " " " "					
225	0.5	No. 3	"	11	17	52.5	13.2	Hard
226	3%	Solution	Corroded in spots	14	14.75	50	17.0	Hard
227	2	Flue	Little corroded	18	13	41.0	15.4	
228	1	Dust	" "	14	13.5	36.75	14.4	
229	0.5	No. 4	" "	13.5	13	32.5	16.2	Hard

TABLE 9 (Continued.)

Plant number		Treatment	Result on Leaf	Length in.	Circumference in.	Weight oz.	Polariscope	Condition at time of analysis
230	3%	Solution	Very badly corroded. See Table 14.					
231	2	Flue	" " "	10	10.5	18	14.2	Hard
232	1	Dust	" " ", but not so extensive	14	13.5	42.5	16	Hard
233	0.5	No. 5	Little corrosion evident	13	14.5	41.5	13.6	Hard
234	3%	Solution	Very badly corroded	14.5	14.5	34.0	15.2	Hard
235	2	Flue	" " "	14	11.5	22.5	17.4	
236	1	Dust	" " "	10.5	13.5	38.5	17	Soft
237	0.5	No. 6	" " "	8	13.75	31.5	16.8	Hard
238	3%	Solution	" " "	9	16.75	51	16	Hard
239	2	Flue	" " "	13	12	30.5	15.8	Hard
240	1	Dust	" " "	10	13	37	16.8	Soft
241	0.5	No. 7	" " " but not so extensive	9.5	14	36.5	13.8	Hard
242	3%	Solution	Little damage if any	11	13.75	41.5	15.8	Hard
243	2	Flue	" " " "	10	17	41.5	14	Hard
244	1	Dust	" " " "	10	10	17	21.4	Soft
245	0.5	No. 8	" " " "	9.5	14.5	38.5	16.8	Hard

In Series No. 3 each sample of dust was mixed with twenty-five or thirty times its weight of water and the plants were sprinkled with the mixture. (Table 11.)

TABLE 11.
Experiments to Determine the Effect of Mixtures of Flue Dust and Water upon Sugar Beets.

Plant Number.	Treatment.	Result on Leaf.	Length.	Circumference.	Weight.	Polariscope.	Condition at time of Analysis.
246	Flue Dust No. 1	Very badly corroded.	14	13.5	42.5	11.0	Hard
247	" " 9	" "	10	10.75	21.0	15.6	Soft
248	" " 2	" "	11	12.75	25	17.2	Hard
249	" " 3	" " but not so extensive	11.5	14.5	41.5	14.0	Hard
250	" " 4	Very badly corroded	10.5	15.0	44.0	15.8	Hard
251	" " 5	Slight injury in a few places	13.0	12.75	31.0	14.8	Hard
252	" " 6	Very badly corroded	9	15.25	39	8.2	Rotten at point
253	" " 7	" "	8	12	27	13.4	Hard
254	" " 8	Uninjured	8	10.5	18	17.8	Hard

One is impressed with the facts that the finely divided "dust" or fume from either a lead or a copper smelter is extremely corrosive in its action upon vegetation, that the gross particles of dust that settle out in flues or chambers near the roasters, blast furnaces, reverberatories etc. are almost without effect upon plants, and that the corrosive power of even the worst materials is neutralized in whole or in part by mixing them with soil. The latter fact fortunately precludes the possibility of the dusts exerting a cumulative action, which would increase the amount of damage from year to year.

Although these plants were treated in August, after they had attained considerable growth, it was deemed wise to collect the beets at the time of the regular harvest in October, measure their length and circumference, obtain their weight and determine their sugar content. For the latter purpose the beet pulp was extracted with water at a temperature of 80° for thirty minutes, clarified with lead acetate and sodium sulphate solutions, cooled to 17.5°. filtered and polarized at that temperature in a Schmidt and Haensch triple field instrument employing a 200 mm. tube. To obtain the percentage of sugar used as a basis of settlement by the Utah Sugar Company at the time these analyses were made, multiply the doubled polariscope readings given in the various tables by the factor 0.90. In Table 12 are given the measurements of some uninjured, untreated beets grown in the field where the main experiments were carried out. In Table 13 we have the results obtained with certain beets grown in a field exposed to the smelter smoke. In this field the visible injury seemed to reach a maximum. Table 14 is given merely for the sake of completeness. It shows the measurements made upon beets whose labels had become somewhat blurred during transit. Table 15 gives a summary of the results upon the beets. All the beets studied were classified as either "injured" or "uninjured", and then the beets of approximately the same weight in the two classes were compared with each other. The results bear out the oft-quoted statement that small beets are richer in sugar than the large ones, and show that the average difference in the sugar content of the "Injured" and "Uninjured" beets is comparatively small. It proves that the yield in tons per acre is a better criterion of damage than the percentage sugar content of the beets.

TABLE 12.

Uninjured Beets Selected for Comparison Purposes.

		L.	Circ.	Weight.	Polar.	
1	Uninjured	10	12.	20.5	17.6	Hard
2	"	13	15.5	46	14.6	Hard
3	"	15	13.25	41	14.8	
4	"	10	13.5	29	18.6	Hard
5	"	12.5	12.5	37	15.6	Hard
6	"	12.5	14.25	38	14	Hard

TABLE 13.

Beets from a Badly Damaged Field, Selected for Comparison Purposes.

		Length.	Circumference.	Weight.	Polariscope.	Condition at time of Analysis.
A	Leaves badly affected	9.5	8.0	10.25	16.4	Soft
B	" "	10	9.5	12.5	17.2	Shrunken
C	" "	7.5	7	6.5	19.0	Soft, shrunken
D	" "	10.5	11.0	17.5	16.6	Hard
E	" "	9.75	9.0	27.75	11.4	Soft, shrunken
F	Uninjured	13	16	61.5	13.2	Hard
G	"	10	11.5	25.0	17.2	Soft, shrunken
H	"	6	7.25	5.5	19.0	Soft
I	"	10	10.5	14.5	16.4	Soft
J	"	7	10.5	14.5	17.0	Hard
K	"	10	12	21.5	16.4	Hard
L	"	9.5	11.0	17.5	17.0	Hard

TABLE 14.

Labels Illegible.

Plant Number.	Length.	Circumference.	Weight.	Polariscope
23 (3) ?	9 in.	11.25 in.	20.5	18
21 ?	12	13.50	29.5	18
2 ? ?	14	13	38.5	15
? ? 4	14	14.5	48	12.8
2 ? ?	15	13.5	38	14.6
25 ?	8	13.75	34	11.0
?	12	17.0	58	11.0
? 9	15	14.5	42.5	15.4

TABLE 15.

Summary of Beet Analyses.

Weight.	Uninjured plants. Number of Plants.	Uninjured plants. Average Polariscope.	Injured plants. Number of Plants.	Injured plants. Average Polariscope.
Less than 15 oz.	13	17.93	5	17.40
15–20	4	16.38	3	17.0
20–25	7	16.74	7	16.51
25–30	7	16.86	3	14.80
30–35	3	16.30	7	15.14
35–40	8	15.15	8	14.70
40–45	8	15.25	7	14.46
45–50	2	15.00	2	16.30
50–55			2	14.60
55–60			1	14.80
60 and over	1	13.2	1	13.20
Average,	53	16.39	46	15.64

Difference in favor of "Uninjured" Beets—0.75%.

In the case of lucerne it has been shown that material that had suffered greatly from the smoke possessed considerable value as forage. An extended series of feeding experiments conducted by L. A. Merrill, late of the Agricultural College of Utah, has proved this.[1] It is evident that a loss in value of a smoke-blighted crop is not necessarily proportional to its loss in beauty.

The appearances of leaves of lucerne and sugar beets grown in the smelter district show that much of the visible injury is entirely analogous to that produced when solid particles of "flue dust" are allowed to fall upon plants. One cannot deny, however, that some of the effects observed when a whole field is blighted within a short time in heavy, moist weather, resemble those produced by sulphur dioxide. By no means is sulphur dioxide to be considered as harmless, especially in an enclosed space and in a moist climate, but we are forced by the weight of the evidence to the conclusion stated in our introduction, *viz.*, that heretofore undue emphasis has been laid upon the injurious effects of sulphur dioxide upon growing plants, and that the harmful action of the solid emanations from the smelters—the so-called "flue dust"—has been seriously underestimated.

In conclusion the author must acknowledge his indebtedness to Messrs. Rawlins, King and Street, attorneys in Salt Lake City, for permission to use much of the matter embodied in this paper; to the Citizens Committee representing the farmers in the recent injunction suit; and to the managers of the Bingham Consolidated Mining and Smelting Company, through whose assistance the work was, in part, made possible. To Mr. W. S. Thomas, consulting chemist of the said company, are due

[1] Western Chemist and Metallurgist, 3, 59 (1907).

the author's sincerest thanks for many suggestions and comments, both as to matter and methods, especially in respect to the problem of injury caused by the solid emanations.

UNIVERSITY OF UTAH,
January, 1907.

PAPERS ON SMELTER SMOKE.

(FIRST PAPER)

The Determination of Arsenic and Other Solid Constituents of Smelter Smoke, with a Study of the Effects of High Stacks and Large Condensing Flues.

BY W. D. HARKINS AND R. E. SWAIN.

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The determination of the constituents of smelter smoke is important for two reasons: many of the constituents have considerable commercial value, while a large number are poisonous in varying degrees to plant and animal life. Under the first class will come sulphur dioxide, sulphuric acid, copper, lead, zinc, arsenic, antimony, and certain other substances. It will be seen that these same substances belong in some degree to ehe second class as well, so that the solution of the problem of recovering the economic values from the smoke will also solve the problem of lessening or preventing its injurious action.

It will be the purpose of a series of articles, of which this is the first, to point out the chemical facts which make the solution of these problems so essential to the welfare of many extensive districts in the west, as well as to some in the east and south of our country. The work which led to the publication of this special article, was the estimation of the amount of arsenic expelled from the greatest of the world's smelters—a plant which has a capacity of ten thousand tons of ore per day, and the output of which for 1906 was estimated as eleven and one half per cent. of the world's production of copper. Compare with this the Freiburg smelters at the time of the work of Haubner[1], Sussdorf[2], Freytag[3], taking the date 1870. At this time the two smelters, the Mülden and Halsbräcken, treated daily about seventy tons of ore. According to Haselhoff and Lindau[4], all the smelters of the Lower Hartz use annually only sixty-three thousand tons, this being the amount for the year 1899. In this country, the Garfield Beach smelter, Utah, is to be enlarged to a capacity of eight thousand tons per day, while the Great Falls, Montana, smelter has now a capacity of three thousand five hundred tons

[1] Haubner, Die durch Hüttenrauch veranlassten Krankheiten des Rindviehes im Hüttenrauchsbezirke der Freiberger Hütten (Arch. f. wiss. u. prakt. Tierheilk. 1878, 4, 97-136; 241-260.)

[2] Sussdorf, Allg. Deut. Naturhist. Ztg., Hamburg, I (1855), No. 3, 97.

[3] Freytag, M., Jahrb. f. d. Berg-u. Hüttenwesen im Königr, Sachsen auf das Jahr. 1873, Abh. 3. ——, (l. c. 1875, Abh. 3).

[4] Haselhoff und Lindau, Rauch-Beschädigung, p. 147.