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A STUDY OF THE REMOVAL OF SULPHUR DIOXIDE FROM LIBRARY AIR

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A STUDY OF THE REMOVAL OF SULPHUR DIOXIDE FROM LIBRARY AIR[1]

By Arthur E. Kimberly[2] and Adelaide L. Emley[2]

ABSTRACT

Tests made in the Folger Shakespeare Library, Washington, D.C., showed that sulphur dioxide, which is harmful to paper, was not completely removed from the air by washing it with untreated water in an air-conditioning system of the usual type. Effective elimination was obtained, however, on washing the air with water that had been treated with alkaline material at a rate sufficient to maintain the hydrogen ion concentration of the wash water within the range pH 8.5 to 9.0. The sulphur dioxide content of the washed air was found to be entirely dependent upon the hydrogen-ion concentration of the wash water. The composition of a mixture of chemicals satisfactory for the treatment of the water is given.

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I. INTRODUCTION

A number of investigations on the extent of atmospheric pollution [3] [4] [5] [6] [7] [8] show that sulphur dioxide is generally present in city air in concentrations great enough to cause damage to vegetation,[9] building materials,[10] and damp cotton fabric.[11]

Experiments on the effect of low concentrations of sulphur dioxide on paper [12] showed that papers exposed to an atmosphere containing sulphur dioxide in an amount varying from 2 to 9 parts sulphur dioxide per 1,000,000 parts of air for 10 days underwent pronounced

[1] This is one of a series of investigations concerning the preservation of written and printed records made at the Bureau of Standards with the assistance of a fund granted for the purpose by the Carnegie Corporation to the National Research Council.

[2] Research Associate, representing the National Research Council.

[3] Smoke Abatement, Report of Committee of Chicago Chamber of Commerce, 1915.

[4] Recent Progress in Smoke Abatement, and Fuel Technology in Manchester, Mellon Institute, Smoke Investigation Bulletin No. 10, 1922.

[5] Meller, H. B., Mech. Engr., vol. 48, pp. 11a, 1275, 1926.

[6] Burrell, B. A., Proc. Leeds Phil. and Lit. Soc. Sci. Sec., vol. 1, pt. 3, p. 116, 1926.

[7] Monnett, Parrott, and Clark, U.S. Bureau Mines Bulletin No. 254.

[8] Monnett, O., U.S. Bureau Mines Technical Paper No. 273.

[9] Clevenger, J. F., The Effect of Smoke on Vegetation, Mellon Institute, Smoke Investigation Bulletin No. 7, 1913.

[10] Papers on the Effect of Smoke on Building Material, Mellon Institute, Smoke Investigation Bulletin No. 6, 1913.

[11] Wilkie, J. B., Laundry "Winter Damage," B.S. Jour. Research, vol. 6, p. 593, 1931.

[12] Kimberly, A. E., Deteriorative Effect of Sulphur Dioxide on Paper in an Atmosphere of Constant Humidity and Temperature, B.S. Jour. Research, vol. 8, p. 159, 1932.

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physical and chemical deterioration, manifested by large increases in brittleness and acidity. In a study of the deterioration of book papers in libraries,[13] it was found that books stored in cities, where atmospheric pollution as high as 1.2 parts sulphur dioxide per 1,000,000 parts of air may be reached,[14] were in a uniformly poorer state of preservation than similar books that had been stored in country or suburban localities where the air was relatively free from sulphur dioxide. As by far the largest number of valuable collections of books are stored in cities, it therefore seemed imperative that some means be found for eliminating sulphur dioxide from the air of libraries.

Control of atmospheric conditions is desirable for the preservation of books and documents also because improper humidities may promote the growth of molds and induce unnecessary weakening of the paper fiber. In an earlier publication,[15] it was recommended that air-conditioning systems be installed in libraries to maintain the conditions of temperature and humidity most favorable to the preservation of paper. It was further suggested that sulphur dioxide might be eliminated from the library air in the process of air conditioning if the wash water were made alkaline by the addition of suitable chemicals. The efficiency of an air-conditioning system of the conventional type with respect to the removal of acid gases, however, was not known. It therefore seemed desirable to learn whether washing air in the customary manner removed sulphur dioxide; and, if not, how the air-conditioning procedure can be modified to provide air for libraries that is completely free from that harmful constituent.

The conductance of the work as planned required the use of a library equipped with suitable air-conditioning machinery. The cooperation of the Folger Shakespeare Library, Washington, D.C., in this respect was secured, as its facilities include an air-conditioning system designed to provide the proper atmospheric temperature and humidity within the stacks and vaults. The Carrier Engineering Corporation, manufacturers of the air-conditioning machinery on which the tests were made, assisted through the services of an engineer, as did the Metropolitan Refining Co., specialists in water treatment.

II. AIR-CONDITIONING EQUIPMENT

A diagram showing the plan of the air-conditioning apparatus is given in figure 1. The spray chamber *A*, where the air is washed and humidified, is a watertight compartment, lined with copper. Inside the enclosed space are two banks of spray nozzles directed toward one another in such a way that the water has good contact with the current of air, but offers little interference to its flow. The water is maintained at a temperature of 50° F. by the admission of cold outside air in winter and by the use of refrigeration in summer. A large glass door, which can be securely clamped down while the apparatus is in operation, gives access to the spray chamber.

[13] Kimberly, A. E., and Emley, A. L., A Study of the Deterioration of Book Papers in Libraries, B.S. Misc. Pub. No. 140, 1933.
[14] Communication from the Bell Telephone Laboratories, New York.
[15] Kimberly, A. E., and Hicks, J. F. G., A Survey of Storage Conditions in Libraries Relative to the Preservation of Records, B.S. Misc. Pub. No. 128, 1931.

The air leaving the water spray is warmed to room temperature by means of the heater *B*, which regulates the temperature of the air delivered to the storage spaces. It is circulated throughout the system by the fan *C*, which has a capacity of about 6,000 cubic feet per minute. On returning from the stack rooms the air is generally rewashed, though, if desired, part of it may be diverted along the bypass *D*, to be combined with the newly humidified air issuing from the spray chamber. In addition, a certain amount of fresh air is constantly admitted to the system at the intake *E*. The quantity either varies automatically with changes in weather conditions, or is kept constant by setting the damper that gives access to the spray chamber. The outside air, then, is drawn through the water curtain with the air being recirculated. In the wintertime, with the fresh air intake automatically regulated, outside air and air returning from the stacks are admitted to the spray chamber in such proportions that the mixture is of approximately the same temperature as the wash water. The temperature of the wash water is kept constant in this way, without the use of steam or refrigeration. If more cold air is admitted than is needed to regulate the temperature, the wash water requires heating

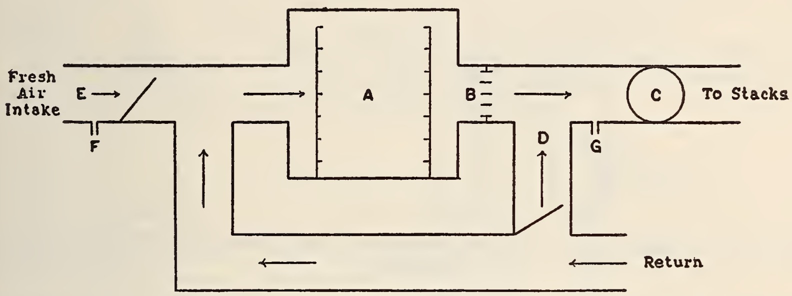

FIGURE 1.—*Diagram of the air conditioning machinery showing outlets F and G from which air for sulphur dioxide tests was drawn.*

to avoid deficiency of moisture in the air delivered to the storage spaces.

For the purposes of this investigation, the dampers which serve to divert the flow of air along the proper channels were controlled by hand. The by-pass *D* was entirely cut off, and all air returning from the stacks passed through the main duct leading to the washer. As much outside air as the system could handle was drawn in, so that the effect of the introduction of polluted air on the wash water would become apparent in the shortest possible time. All of the air used, outside air and that returning from the stack room, was passed through the washer immediately prior to its admission to the storage spaces.

III. EXPERIMENTAL DETAILS

To determine the actual efficiency of such a system for the purification of library air, an apparatus for the estimation of small amounts of sulphur dioxide in air—that is, 1 part or less in 1,000,000—was installed in the fan room of the library. Connections were so arranged with lengths of glass tubing that samples of air for test might be drawn alternately from the air-conditioning system at the points *F* and *G* illustrated in figure 1. Incoming air drawn from *F* was made up wholly of unwashed outside air; washed air, from the outlet *G*, had been, before its contact with the water sprays, an untreated mixture of air returning from the stack room and fresh incoming air. The results of alternate tests showed the relationship of the sulphur dioxide content of this washed air to that of the incoming untreated air.

The method used for the determination of sulphur dioxide in this investigation was a modification of the procedure developed by S. W. Griffin and W. W. Skinner.[16] It is claimed that under ordinary field conditions the method is accurate to ± 0.02 part sulphur dioxide per 1,000,000 parts of air. It depends upon the absorption of sulphur dioxide in excess iodine solution containing starch, and the addition of iodine to this solution until the original color is restored. The amount of iodine added, when corrected for iodine mechanically removed by bubbling, is a measure of the sulphur dioxide present in the air.

The apparatus, which is illustrated in figure 2, consists of: *A*, a flowmeter of the orifice U-manometer type; *B*, the absorber (approxi-

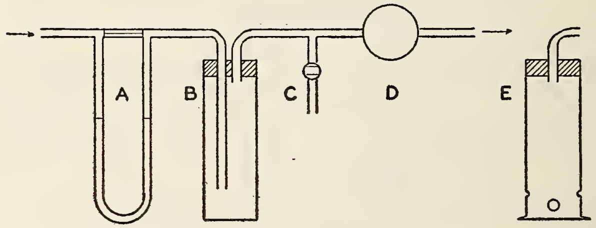

FIGURE 2.—*Apparatus for the determination of small amounts of sulphur dioxide in air.*

mately 1.5 inches by 11.5 inches, inside dimensions); *C*, a valve to regulate air passing through *A*; and *D*, a small centrifugal pump.

The procedure is as follows: A measured quantity (usually 1 ml) of 0.001 *N* iodine solution (containing 25 g recrystallized potassium iodide per liter) is added to a mixture of 80 ml of distilled water and 20 ml of starch solution (1 g soluble starch and 2 g potassium iodide per liter) in the absorber. At the same time a duplicate mixture is prepared in a 300 ml Erlenmeyer flask for use as a color standard. Air is then drawn through the solution in the absorber until approximately 30 liters have been passed. This solution is then transferred to a 300 ml flask and 0.001 *N* iodine added to it in measured amounts until its color matches that of the standard solution. The amount of iodine solution added, when corrected for iodine mechanically removed by air bubbles, is a measure of the quantity of sulphur dioxide in the air examined. The amount mechanically removed is easily determined by connecting a tower, *E*, (fig. 2) which is about 12 inches high, filled with soda lime, next to the flowmeter in such a manner that all air passing through the absorbing solution is first freed from sulphur dioxide by contact with soda lime, and repeating the test procedure

[16] Griffin, S. W., and Skinner, W. W., Small Amounts of Sulphur Dioxide in the Atmosphere, Ind. Eng. Chem., vol. 24, p. 862, 1932.

described above. The amount of iodine necessary to restore the original color is equal to that mechanically removed by the air bubbles, which varies with the time of air flow and with the temperature of the air.

The hydrogen-ion concentration [17] of the wash water in the air-conditioning system was frequently determined colorimetrically in order to find the relationship, if any, between the amount of sulphur dioxide in the washed air and the hydrogen-ion concentration of the wash water. This relationship assumed special significance after the initiation of the alkaline treatment of the wash water.

The alkalinity of the wash water was increased by the addition of a mixture of chemicals which form a passive gelatinous deposit [18] upon metal surfaces thereby retarding corrosion due to contact with water. In localities where a high degree of atmospheric pollution is encountered, the metal parts of air-conditioning systems corrode so rapidly, if preventive measures are not taken, that complete replacement has in certain cases become necessary after less than a year of operation. The hydrogen-ion concentration of the wash water in one system, where rapid deterioration was noted, dropped from pH 7.4 to pH 6.0 in the course of 8 hours' operation due to the absorption of acid from the air washed. The necessity of protection against corrosion is very evident.

An analysis of the alkaline material used in this study, which was recommended by the makers of the air-conditioning equipment and which may be obtained commercially, follows:

Color		amber
Odor		indefinite
Condition		cloudy liquid
Loss on ignition	percent	59.2
Sodium silicate	percent	28.3
Sodium hydroxide	percent	3.1
Sodium carbonate	percent	3.2
Sodium dichromate	percent	4.9
Trisodium phosphate	percent	1.0
Total alkalinity	percent	10.9 (calculated as Na_2O)
Water insoluble		trace

No study of the material except as to its ability to absorb sulphur dioxide was made. This material was added continuously to the wash water at a rate sufficient to maintain the hydrogen-ion concentration of the water within the range pH 8.0 to 9.0. The amount added was regulated by a by-pass gravity feeder located on the pressure side of the pump that circulates the wash water.

A day's work usually comprised 20 to 25 determinations of sulphur dioxide, including several blanks and the tests of washed air and incoming air; 4 determinations of relative humidity; 2 of barometric pressure; and 4 of the hyrogen-ion concentration of the wash water.

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[17] Hydrogen-ion concentration, which is a measure of the acidity or of the alkalinity of any solution, is commonly expressed by means of a scale running from pH 0.0 to pH 14.0. Solutions which exhibit hydrogen-ion concentrations below pH 7.0 are said to be acid, while those possessing hydrogen-ion concentrations above pH 7.0 are said to be alkaline. The degree of acidity or of alkalinity of any solution is indicated by its position on this scale relative to the neutral point (pH 7.0). For example, a solution of pH 1.0 is more acid than one of pH 6.0 and a solution of pH 14.0 is more alkaline than one of pH 8.0.

[18] Hoar, T. P., and Evans, U. R., Passivity of Metals VII—Specific Function of Chromates, J. Chem. Soc., pp. 2476–2481, 1932.

IV. RESULTS

Figure 3 gives the average results of the experimental work, day by day, over a period from January 6 to February 16, 1933. It compares the sulphur dioxide content of the untreated air entering the library with that of the washed air inside, with reference to the effect of washing with untreated water and water treated with the alkaline mixture. Figure 3 also shows the three successive changes or different treatments of the wash water, with the varying hydrogen-ion concentrations which characterized them. From January 6 to 24, the wash water was untreated and unchanged, though enough fresh water was continuously added to make up for the amount lost

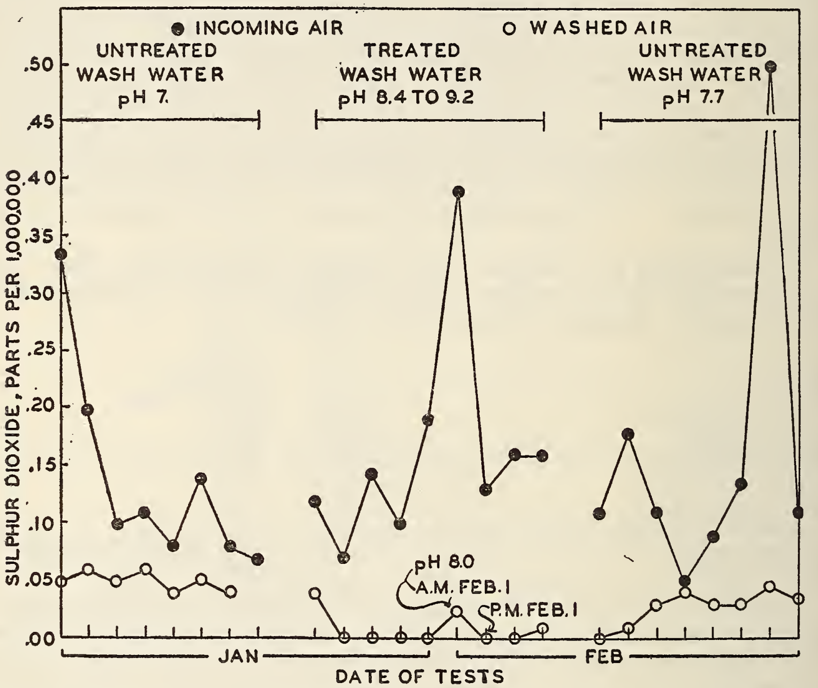

FIGURE 3.—*Comparison of the effect of washing with untreated and treated water on the sulphur dioxide content of library air.*

by evaporation. During this period the hydrogen-ion concentration averaged pH 7. From January 25 to February 4, the water was treated with suitable additions of the alkaline mixture already described, at a rate such that the hydrogen-ion concentration of the resulting solution fell only momentarily below pH 8.6. On February 6, the system was drained completely and refilled with fresh, untreated water of pH 7.7.

The results of some of the individual tests for sulphur dioxide, from which the averages of figure 3 were compiled, are given in table 1. The complete test data for 4 representative days are shown. The results of the first day, in the first division of the table, are illustrative of all the analyses carried out in the stack room, when the air had been washed with untreated water. They indicate the presence of an appreciable quantity of sulphur dioxide in contact with the library books.

TABLE 1.—*Sulphur dioxide content of library air*

Stack-room air		Incoming air								
Untreated wash water Dec. 16, 1932		Untreated wash water Jan. 16, 1933			Treated wash water Jan. 31, 1933			Untreated wash water Feb. 13, 1933		
Time	Sulphur dioxide	Time	pH of wash water	Sulphur dioxide	Time	pH of wash water	Sulphur dioxide	Time	pH of wash water	Sulphur dioxide
		Unwashed air [1]								
a.m.	*Parts per million*	*a.m.*		*Parts per million*	*a.m.*		*Parts per million*	*a.m.*		*Parts per million*
9.50	0.09	9.50		0.55	9.45		0.37	10.30		0.12
9.55	.07	9.55		.53	10.00		.37	11.00		.09
10.00	.08	10.20		.46	10.40		.09	11.45		.17
10.10	.09	10.50		.33	11.30		.11	*p.m.*		
10.45	.05	11.40		.36	*p.m.*			2.00		.17
11.35	.05	*p.m.*			1.35		.07	3.00		.14
11.45	.07	1.55		.16	4.10		.12	4.00		.12
11.55	.07	2.25		.15						
p.m.		3.30		.31						
1.35	.05	3.35		.28						
1.45	.05	4.00		.21						
2.15	.07									
2.20	.06									
3.40	.05	Washed air [2]								
3.45	.05									
		a.m.			*a.m.*			*a.m.*		
		10.15	7.1	0.04	9.55		0.00	10.20	7.7	0.02
		10.45		.04	10.10	9.2		10.55		.01
		11.50		.06	10.30		.00	11.10		.02
		p.m.			11.45		.00	11.25		.03
		2.00		.06	*p.m.*			11.35	7.7	.03
		2.40		.05	1.50	8.9	.00	*p.m.*		
		3.45		.06	4.20	8.6	.01	2.15		.04
								2.35		.04
								2.55		.04
								3.50		.04

[1] Analysis of air drawn from outlet *F*, fig. 1.
[2] Analysis of air drawn from outlet *G*, fig. 1.

The upper groups of the other divisions of table 1 give the data derived from sulphur dioxide determinations made on the incoming untreated air. The results of these 3 days are clearly indicative of the general trend. As a rule, the sulphur-dioxide content of the air coming in from outside was changing continually, being highest in the morning, lowest about noon, and rising toward evening. The lower groups give the sulphur-dioxide content of the mixture of outside and return air that had been washed with either untreated or treated water.

From the data contained in figure 3, as well as from table 1, it is apparent that air washed with untreated water in an air-conditioning system of the customary type, though containing less sulphur dioxide than unwashed air, was still appreciably contaminated. Figure 3 shows that complete elimination of sulphur dioxide was effected by washing air with treated water. Although the sulphur-dioxide content of the outside air varied from hour to hour and day to day, the amount of sulphur dioxide present in the air after washing was found to be entirely dependent upon the hydrogen-ion concentration of the wash water. Figure 4 illustrates this relationship. As the alkalinity of the wash water decreased, due to the absorption of sulphur dioxide coupled with insufficient additions of the alkaline material, the amount of sulphur dioxide in the washed air rose. Air treated with water having a hydrogen-ion concentration greater than pH 8.6 was com-

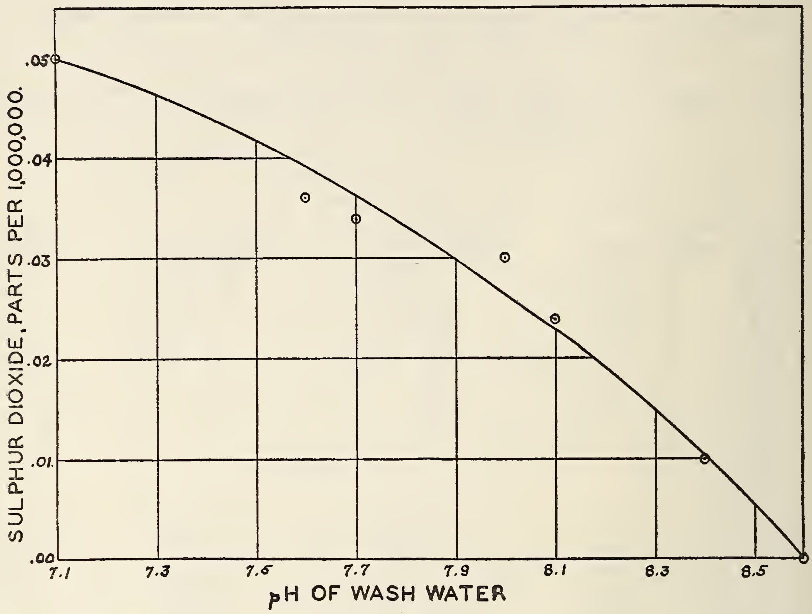

FIGURE 4.—*Relationship of the sulphur dioxide content of washed air to the hydrogen-ion concentration of the wash water.*

pletely free from sulphur dioxide, and, in that respect, suited to use in libraries.

V. RECOMMENDED PRACTICE

To maintain the most favorable storage conditions for the preservation of paper, it is recommended that libraries, particularly in localities where a high degree of atmospheric pollution is encountered, be equipped with air washers; or, better, air-conditioning systems. To effect complete removal of sulphur dioxide from the air, the water in the air washer should be changed at least once a week and treated continuously with an alkaline solution, so that the hydrogen-ion concentration of the wash water may always fall within the range pH 8.5 to 9.0. The hydrogen-ion concentration should not be allowed to rise above pH 9.0 due to the danger of removing zinc from brass fittings. All air returning from the storage spaces should be rewashed to eliminate the chance of recirculating any sulphur dioxide that might have leaked into the system. It is considered best to run the entire air-conditioning apparatus continuously. If these precautions for the purification of air for libraries are observed, it is believed that the life and usefulness of the material stored will be considerably prolonged.

VI. SUMMARY

1. An air washer of the conventional type using untreated water did not completely remove sulphur dioxide from library air.

2. Sulphur dioxide was completely eliminated from library air by washing with water to which sufficient alkaline material had been continuously added to maintain the hydrogen-ion concentration of the water within the range pH 8.5 to 9.0.

3. The composition of a specific mixture of chemicals, which is commercially available and which was found to be satisfactory in the treatment of the wash water, is given.

VII. ACKNOWLEDGMENT

The assistance of W. A. Slade, W. S. Tyler, Jr., J. J. Murphy, and C. W. Sauerhoff of the Folger Shakespeare Library, and W. H. Carter of the Carrier Engineering Corporation, C. M. Stern of the Metropolitan Refining Co., and W. L. Holt [19] throughout this work is hereby gratefully acknowledged.

WASHINGTON, *July 8, 1933.*

[19] Assistant Research Associate, representing the National Research Council.

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