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BY R. L. MARKS AND C. R. HUTCHCROFT

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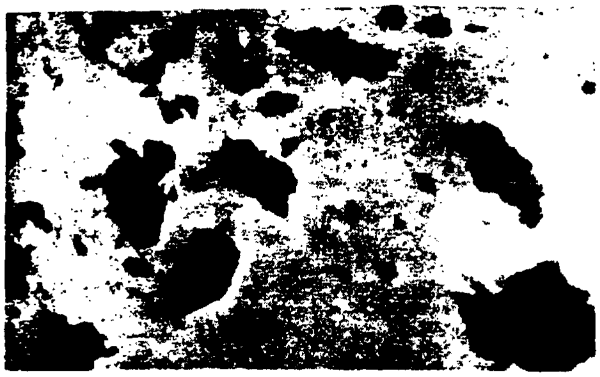

Fig. 1. Electron microphotographs of calcium silicate hydrate compounds (binders). Top, normal cured. Bottom, autoclave cured

Resistance of asbestos-cement pipe to corrosive soil conditions

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Mr. Marks is staff manager, Johns-Manville Corp., New York, N. Y., and Mr. Hutchcroft is technical service manager, Certain-teed Products Corp., Ambler, Pa. This joint effort was reviewed by technical personnel of the Asbestos-Cement Pipe Co. and the Flintkote Co.

Asbestos-cement pipe is non-metallic in composition and, therefore, not subject to the same mechanics of corrosion as are evidenced by most ferrous metal products. A difference in corrosion resistance and chemical resistance characteristics also exists between autoclave-cured asbestos-cement pipe and normal-cured concrete pipe; asbestos-cement pipe produced in the United States is cured at high temperatures and pressures, reducing the incidence of free lime in the finished product by 10 to 30 times. High temperature steam curing makes asbestos-cement a more chemically stabilized cement product.

This paper discusses the properties of asbestos-cement pipe and its performance characteristics under actual conditions in service. For background information, and to place asbestos-cement pipe in perspective within the framework of the piping industry as a whole, a brief outline of general manufacturing methods, history, and usage is presented.

IT IS HELPFUL to look upon the asbestos-cement silica system as a composite material consisting of a matrix or binder reinforced with asbestos fiber. The asbestos fiber contributes to the high tensile and impact strength of the product. The portland cement-silica is the binder for this system, and the products formed on curing are largely responsible for the chemical resistance of the product.

The chemical reactions that take place during the setting of portland cement are very complex, and the final reaction products produced during autoclaving are substantially different from those produced by the normal curing process.

Because different chemical reactions take place in the autoclaving and the normal curing processes, different ingredients are used for each type of product. A typical normal cured asbestos-cement product contains approximately 20 percent asbestos fiber and 80 percent portland cement. A typical autoclave cured product contains 20 percent asbestos fiber, 40 to 50 percent portland cement, and 30 to 40 percent silica flour.

The binder in a normal cured formulation (about 28 days in water) consists of a poorly crystallized gel of hydrated calcium silicate (CSH-I gel) and up to 15 percent calcium hydroxide. The calcium hydroxide is released from the portland cement during the hydration process and is the principal cause of the poor chemical stability of normal cured asbestos-cement products.

The binder produced by the autoclaving process is microcrystalline hydrated calcium silicate (tobermorite). The chemical composition of this binder is not greatly different from the binder formed in the normal curing process, but the improved crystallinity of the autoclaved binder (tobermorite) over the amorphous normal cured binder results in a greater chemical resistance. The electron microphotographs of the two types of binder are shown in Fig. 1.

The most significant feature of the autoclaved product is the absence of any appreciable amount of free calcium hydroxide. Under autoclave conditions, the free lime produced by the hydration of the cement reacts with the silica flour to form additional tobermorite. Silica flour is not commonly used in the normal cured formulations because it does not react with the calcium hydroxide at ambient conditions.

Soil exposure

Soil exposure means potential corrosion by soils. Each year millions of dollars and much effort are consumed in preventing or retarding attack of underground piping systems by corrosive soils.

Typically, pipe is buried in the soil to transport liquids and to act as protection to other materials (such as electrical or telephone cable). The choice of piping materials and means of protecting those materials is dictated by the nature of the soil in which the pipe is to be installed. An obvious first choice is a material that offers economy of installation and operation, strength, and a wide range of resistance to soil environments without requiring costly and complicated protective measures.

Soils may be divided into two broad categories: natural soils are those that have been produced by purely natural means and are undisturbed other than for installation of pipe. Artificial or manmade soils are those produced, for example, by the disposal of various wastes, dredging operations, or other land fill, or by leveling or elevating operations.

Likewise, corrosive tendencies of soils may be divided into two broad categories: naturally corrosive soils have a basic natural composition that provides an environment inimical to piping materials. Such characteristics as sulfate content, bacterial activity, acid content, compaction, mineral content, etc., cause soils to be naturally corrosive. Induced corrosive potential is caused by man's actions in waste disposal, topography alteration, etc., which have either produced an environment corrosive to piping materials or have enhanced an already corrosive soil environment.

As knowledge of soil-induced corrosion has become more widespread, terms such as redox potential, cathodic protection, electrolysis, and galvanic action have become common. These terms are used in connection with the subject of corrosion of an electrical or electrochemical character. Corrosion of this type is produced by or produces a flow of electrical current. It relies upon such electrical effects as electrolysis, galvanic action, certain forms of bacterially-associated electrical activity, soil aeration, electrolyte activity, etc. This type of corrosion is important in pipes composed of electrically conductive materials, but it has no real bearing on non-metallic, non-conductive piping materials such as asbestos-cement.

Acid soils

Certain types of soil or soil conditions can, however, have an effect upon asbestos-cement pipe as well as on metallic piping. Soils that contain acids, for example, will tend, by chemical action, to attack asbestos-cement pipe as well as metallic pipe, but the attack on the former does not involve electrolytic corrosion.

Hardened portland cement silica, which forms the binder in autoclaved asbestos-cement pipe, is composed of many complex silicate structures, all of which are alkaline in nature. These al-

Asbestos-cement pipe—What it is

The first patents for asbestos-cement pipe were granted in 1913 in Italy, where equipment was installed and production started. By 1921, asbestos-cement pipe was well accepted in Europe. In 1929, Johns-Manville Corp. acquired rights to manufacture and sell asbestos-cement pipe, and the first length was made in the United States in September of that year.

In many applications, asbestos-cement pipe gradually superseded other pipe materials because of its good performance, economic installation, and other characteristics. Steady growth followed, both abroad and in the United States.

Continued product improvements such as high pressure steam curing (autoclaving) and tighter, more easily assembled joints, created increasing demands for increased production and additional plants. There was further expansion from water pressure pipe to sewer, building sewer, telephone and electrical ducts, gas vent pipe, industrial vent pipe, stacks, irrigation pipe, air duct, underdrain and storm drain pipe applications. In 1938, the Keasbey and Mattison Co., now Certain-teed Products Corp., entered the industry, followed by the Flintkote Corp. in 1963 and Cement Asbestos Products Co. in 1965, bringing further expansion. Today, hundreds of thousands of miles of asbestos-cement pipe are in service throughout the United States.

Composition

Asbestos-cement pipe is made by combining the basic raw materials—asbestos, portland cement, silica, and water—using modern manufacturing techniques. The asbestos is separated into fibers, which provide high tensile strength reinforcement to the pipe. The fibers are batch mixed with cement and silica flour in the dry state, water is then added, forming a slurry, which is agitated to assure uniformity. The slurry is deposited on a wide, endless belt where it is carried to the pipe-forming section of the machine as shown in the accompanying flow sheet. Here it is transferred under pressure to a steel mandrel as a continuous sheet wound up to form a high-density homogeneous pipe throughout its thickness and length.

The pipe is released from the mandrel, and after an air curing period, is placed in high presssure steam curing tanks (autoclaves) for final curing. After autoclaving, the pipe is trimmed and machined to required dimensions for jointing, then inspected, tested, and packaged for shipment. Asbestos-cement pipe couplings are manufactured by the same process as the pipe.

Autoclaving process

The durability of cement-based structures has been of great concern since the Roman days. The very nature of pipe applications demands a material that has a long operating life and requires a minimum of maintenance and repair. This requirement is, of course, in addition to the usual ones of high strength and dimensional stability. The adoption of high pressure steam curing (autoclaving)[1] by the American asbestos-cement pipe industry was the culmination of a search for a curing method that would give rapid strength development and improve the chemical stability of the products.

The autoclaving process refers to the curing of portland cement products in a saturated steam atmosphere at a temperature above the normal boiling point of water. The process is generally carried out in the temperature range of 325 to 385°F, with pressures of about 80 to 200 psi. A period of pre-curing, prior to autoclaving, in a moist atmosphere of ambient pressure is used to increase handling strength. The total time required for atmosphere and autoclave curing will range up to 48 hr.

In contrast to the above autoclaving method, the so-called "normal curing" process requires 20 to 30 days, with the product either in a moist atmosphere or under water. In addition to the rapid strength development, the autoclaved cured products have the following advantages:

Increased resistance to sulfate and other chemically aggressive environments.

An approximate 50 percent reduction in the volume change that takes place during the wetting and drying of the product.

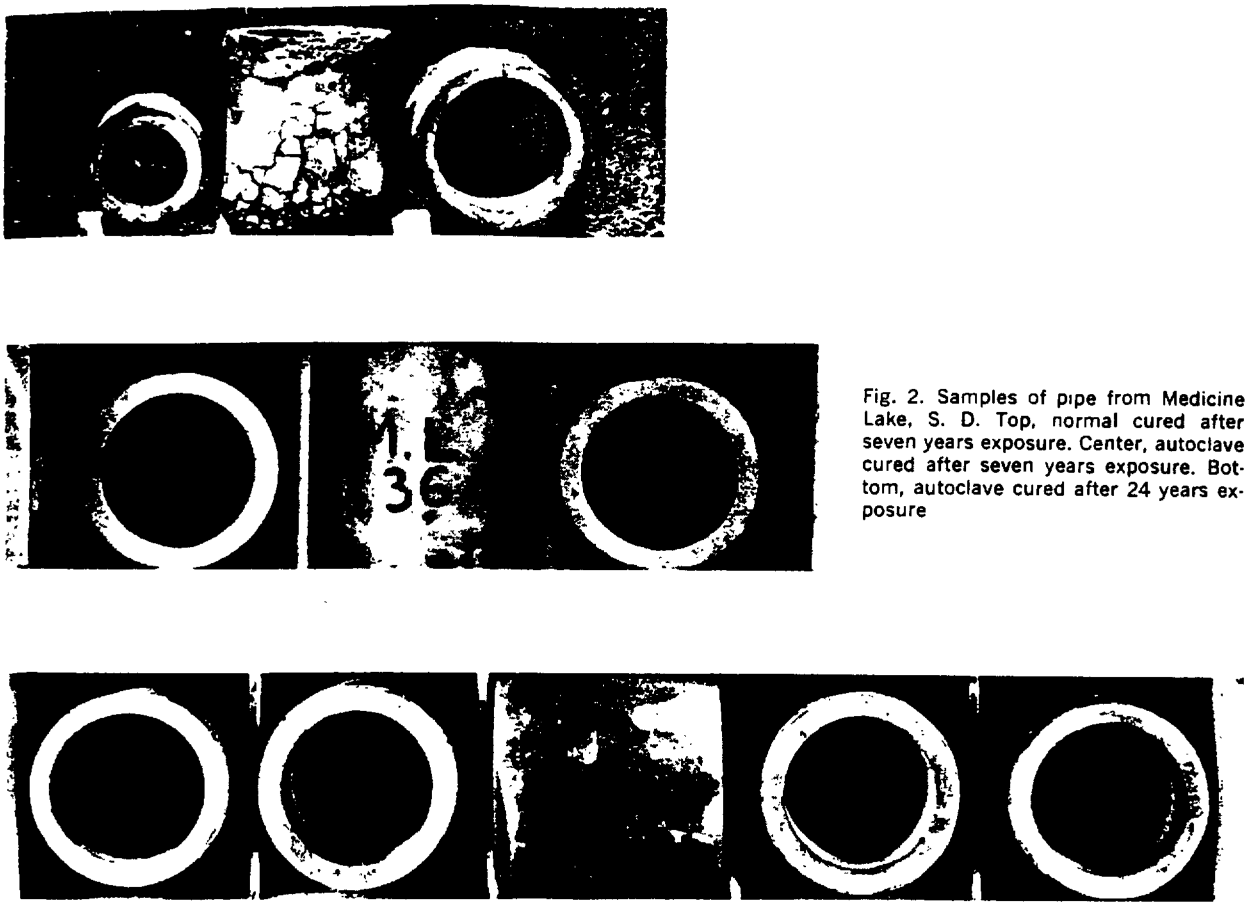


Fig. 2. Samples of pipe from Medicine Lake, S. D. Top, normal cured after seven years exposure. Center, autoclave cured after seven years exposure. Bottom, autoclave cured after 24 years exposure

kalis react with the acid in the soil, causing some of the silicate materials to be chemically altered. Mere presence of acid, however, is not the determining factor in such chemical corrosion; corrosion is dependent upon the amount and type of acid. Many soil acids are only weakly ionized, i.e., their effect upon pH is slight, and most soil acids are weak organic acids rather than stronger inorganic acids.

Except for sulfuric acid, strong acids are rarely found to occur naturally in soils because they are too reactive and water soluble. Mine drainage water is generally strongly acidic, with pH values often ranging down to 1.5 or 2.0, because of the presence of sulfuric acid. Such acid mine waters, when percolating through soil, produce low soil pH values in the range of 3.5 to 5.5. Decomposition of organic matter in swamps and salt marshes can also produce acidic conditions. It becomes apparent that neutralization of alkaline constituents in asbestos-cement materials by soil acids is theoretically possible. The amount of readily available soil acid, as denoted by the pH, is the determining factor in such chemical corrosion.

The conclusion could be reached from the above that any condition in which the pH is below the neutral point (7.0) could lead to chemical attack; this is not, in fact, the case. Considering that the amount of acid attack is the governing factor in the overall service life of an asbestos-cement pipe, one may then ask the relationship between performance life and acid concentration. Test sample burials reported by the National Bureau of Standards[2] for periods up to 12 years in soils of pH as low as 4.3 show only a negligible effect on asbestos-cement pipe in such environments. Actual in-service installations under similar acid conditions for 20 to 25 years substantiate these findings. The type of soil plays as large a part in chemical aggression as does its acid concentration.

The reaction of an acid with an alkaline material produces a salt of that acid. The nature of the salt produced has substantial effect upon the life of the alkaline material in its acidic environment. The corrosive effects of two strong acids, hydrochloric and sulfuric, present in equal concentrations can be compared as follows: Nearly all the salts produced by the reaction of hydrochloric acid with alkaline materials are very soluble in water. When such salts are formed upon contact of this acid with asbestos-cement pipe (calcium chloride), they are carried away from their site of formation.

While the same reaction (i.e., neutralization) will take place between sulfuric acid and asbestos-cement pipe, the salt produced, gypsum, is only sparingly soluble in water and so usually remains where it is formed. Its presence slows down the rate of attack, substantially prolonging the service life of the product. Most of the common organic acids found in soils also produce salts that are sparingly soluble and duplicate the effect noted above. The fact that most of these organic acids are weak acids produces further retardation of reaction and prolongation of life.

Low hardness waters

Waters of very low hardness (i.e., low levels of calcium and magnesium content) tend to extract calcium and magnesium from materials rich in these constituents. Asbestos-cement pipe is composed of complex calcium silicates and hence may be expected to release

TABLE 1—FREE LIME CONTENT AND SULFATE RESISTANCE OF NORMAL AND AUTOCLAVE CURED CEMENTS

Type of cure	Silica/cement	Cement type	Free lime (%)	Sulfate resistance: expansion (%)*
Autoclave, 125 psi, 16 hr	0.6/1.0	I	0.4	0.03
		V	0.5	0.03
Normal, underwater 28 days	0.0/1.0	I	15.5	0.16
		V	13.7	0.11

*U. S. Bureau of Reclamation sulfate resistance test; measures expansion after 28 cycles.

TABLE 2—$Ca(OH)_2$ CONTENT AND EXPANSION OF NORMAL AND AUTOCLAVE CURED CEMENTS

Product	Curing	$Ca(OH)_2$ (%)	Expansion in Na_2SO_4 sol'n. at given age (%)		
			28 days	3 months	8 months
Asbestos-cement	In water, 28 days	9.6	0.047	0.080	0.113
Asbestos-cement silica	High pressure steam	0.2	0.019	0.030	0.037

TABLE 3—EFFECT OF AUTOCLAVING ON SULFATE RESISTANCE

(Mix contained by weight): 1 part portland cement A, 1 part ground sand,* 6 parts 18 to 25 mesh sand

Curing	Storage solution	Length of storage (weeks)	Expansion (%)
7 days, water, 18°C	Na_2SO_4	8	0.49
	$MgSO_4$	8	0.49
Autoclaved, 7 hr, 183.5°C	Na_2SO_4	200	0
	$MgSO_4$	200	0

* Through 170 BS mesh

calcium to a soft or calcium-starved water. While such can be the case, the likelihood of calcium-starved water being present in a soil is slight because contact with the soil will increase the hardness. Furthermore, such water in a soil in contact with an asbestos-cement pipe would tend to be quiescent, i.e., not flowing. As such a quiescent soft water picks up calcium, its softness, and hence its aggressiveness, is reduced. Certain gravelly or sandy areas subjected to high rainfall or runoff may produce soft water leaching of calcium from calcium rich materials.

A soil's physical characteristics may also play a part in its corrosivity. Aeration of a soil affects the availability of oxygen and moisture and is dependent upon such physical characteristics as apparent specific gravity, particle size and distribution, and moisture content. Localized differences in these characteristics lead to differential aeration. This results in the formation of oxygen concentration cells, wherein low oxygen areas become anodic (sites of corrosion) compared to sites along the same conductive pipeline where oxygen is more accessible.

A manmade soil or foreign material in a natural soil can often be more corrosive than a purely natural soil. Direct addition of some waste materials produces acids upon decomposition and creates acidic soil conditions that can be detrimental to piping materials.

Sulfate environmental effects

Sulfate soils, natural or manmade, provide another corrosion potential, both to metals and to materials composed of portland cement Extensive research has been carried out in the laboratory and in the field to determine the main causes for the attack of asbestos-cement products in a sulfate containing environment. In general, the sulfate environment will react readily with the free calcium hydroxide or slowly with the available calcium in the loosely bound, poorly crystallized CSHI binder gel, to form gypsum $(CaSO_4 \cdot 2H_2O)$ and/or ettringite $(3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O)$, a complex salt of sulfate and cement clinker component $3CaO \cdot Al_2O_3$, accompanied by volume expansion in both cases.

This research has also included a search for ways of protecting the asbestos-cement product from this type of chemical attack. Two interesting field tests, a laboratory study, and other available data illustrate that autoclaved asbestos-cement pipe is more sulfate resistant than normal cured pipe.

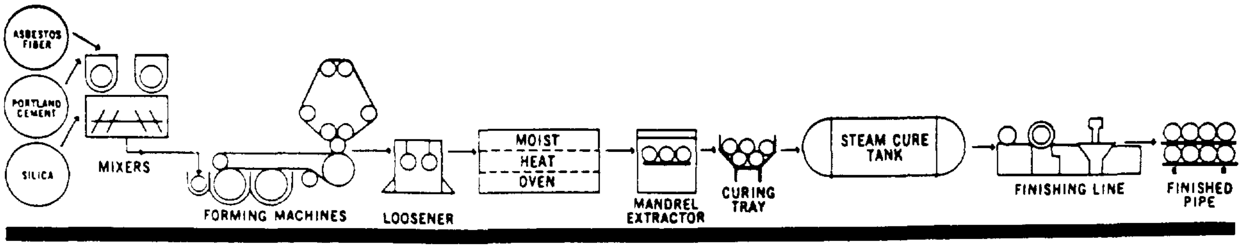
Medicine Lake studies.[3,4] Asbestos-cement pipe cured by both normal and autoclave techniques was exposed to the waters of Medicine Lake, S. D., for periods up to 24 years. This water is exceptionally aggressive to ordinary cement products because it is high in sulfates (5 to 8 percent) with two-thirds of the total salt as magnesium sulfate, one-quarter as sodium sulfate, and the remainder a mixture of several salts present in minor quantities.

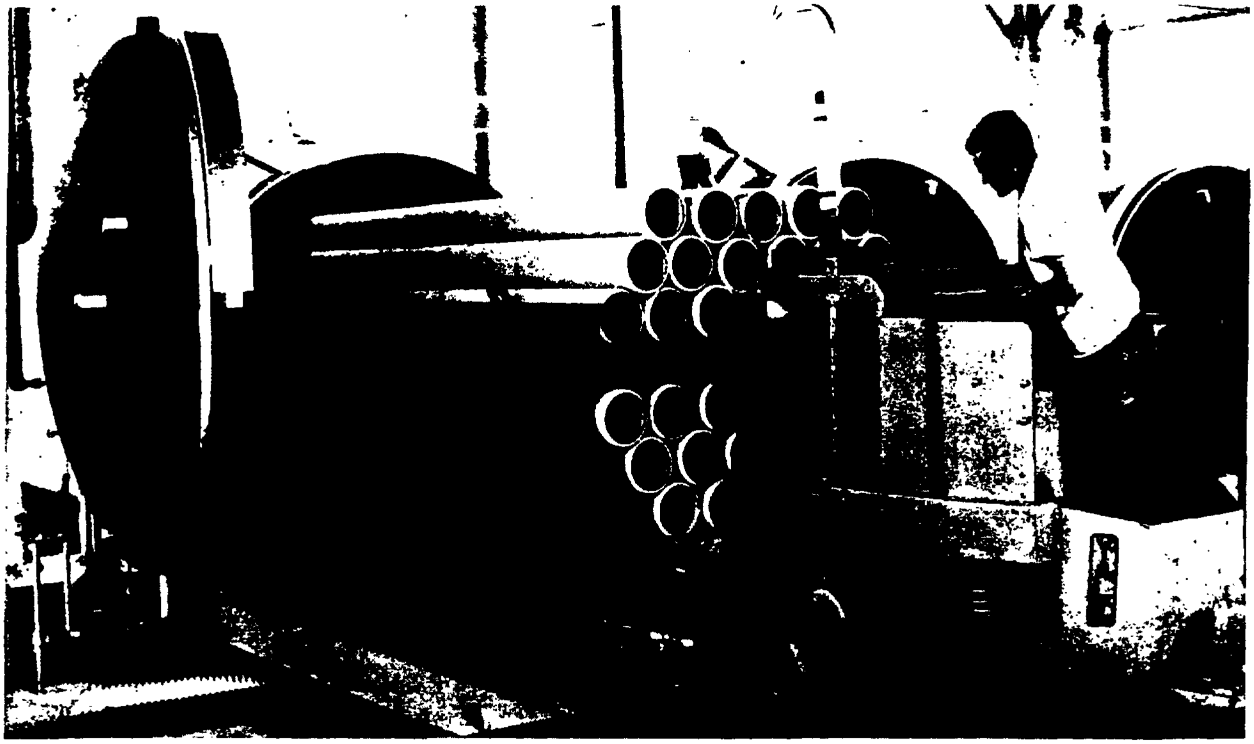
The sulfate expansion of normal cured pipe and autoclaved pipe exposed to this severe environment is shown in Fig. 2. At the end of seven years, the normal cured pipe was badly deteriorated, while after 24 years, the autoclaved pipe showed essentially no attack.

The badly deteriorated condition of the normal cured material in the later years made it possible to obtain meaningful compressive test results. However, an interesting aspect of the autoclaved sample was the increase in compressive strength from 8320 psi at one year to 14,590 psi after 24 years, an increase in compressive strength of more than 77 percent.

Manson[4] concludes in his report, "it should be emphasized that any concrete that gives a high strength after 10 years exposure to the sulfate waters of Medicine Lake can be classified as highly sulfate resistant. Any

Simplified flow diagram of asbestos-cement pipe manufacture





Asbestos-cement pipe being placed in an autoclave for curing

concrete that gives a good test after 20 years exposure to the sulfate waters of Medicine Lake can be classified as an extremely high sulfate resistant concrete."

Certainly the performance of the autoclaved asbestos-cement pipe samples warrants its classification as a product with extremely high sulfate resistance.

Ordway studies.[4] In 1934, a normal cured asbestos-cement pipeline was installed in Ordway, Colo., an area that has high sulfate content soil conditions (2 to 3.0 percent SO_3). Approximately six years after installation, the deterioration of pipe wall in spots caused leaks and ruptures in the line. Microscopic examination of the affected portion of the pipe showed bands of a fibrous crystallation material (ettringite, $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$), running perpendicular to the bands. This compound is formed by the reaction between free calcium hydroxide, portland cement, and the sulfate environments, and is usually accompanied by large volume expansion.

As these breaks occurred in sections, new lines of autoclaved asbestos-cement pipe replaced the old material. The entire replacement was completed within 13 years. Inspection in 1960 showed no visible evidence of sulfate attack nor failure of the autoclaved product.

Laboratory data. Yang and Blair[5] tested sulfate resistance of asbestos-cement pipe using normal and autoclave curing Type I (general purpose) and Type V (high sulfate resistance) cements in each process. Table 1 shows that Type I cement with autoclaving is as sulfate resistant as the Type V with autoclaving and that autoclaving in either case is superior to normal curing. In addition, the amount of free lime is reduced by autoclaving.

Literature data. Committee C-17[6] of ASTM confirmed by test that autoclaving reduced uncombined calcium hydroxide and reduced expansion of autoclaved vs. normal cured products when subjected to a sulfate medium as shown in Table 2.

Lea's paper[7] provides excellent data on the effect of high pressure steam curing on the sulfate resistance of mortars with ground silica sands, as shown in Table 3.

Sulfate resistance of asbestos-cement products is determined by the chemical stability of the cement binders. Autoclaved formulations with autoclave curing insure a more resistant pipe by:

Removing free lime, which is susceptible to sulfate attack.

Forming stable calcium silicate binder tobermorite of crystalline form.

Minimizing the volume changes and maintaining structural strength.

Forming stable binder material, which is also more chemically resistant than the binder of normal-cured asbestos-cement products.

The National Bureau of Standards field test[2] involving exposure to a wide range of soils at 15 test sites was conducted for periods up to 13 years. These soils ranged in pH from 2.6 to 9.4, resistivity measured from 84 to 17,800 ohm-cm, and the amount of air present covered a wide range. The summary of this study states: "even under the most adverse conditions to which the specimens were exposed, the bursting and crushing strengths of all of the samples after exposure were considerably higher than the requirements of the Federal Specification for Asbestos-Cement Pressure Pipe." ☐☐

REFERENCES

1. Washa, G. W., *J. Am. Concete Inst.* **62**:869 (1965).
2. Romanoff, M. and Denison, I. A., *Corrosion* **10**(5):169 (1954).
3. Miller, D. G. and Manson, P. W., "Long Time Tests of Concretes and Mortars Exposed to Sulfate Waters." Tech. Bull. 194, Minneapolis Agricultural Experimental Station, 1-111 (1951).
4. Manson, P. W. and Blair, L. R., *Mat. Res. and Stds.* **2**(10):828 (1962).
5. Blair, L. R. and Yang, J. C., *In* Proc. of the Fourth International Symposium, Chemistry of Cements, Washington, D. C., 1950.
6. Lerch, W., "Chemical Stability of Asbestos-Cement Products." National Bureau of Standards Monograph No. 43, Washington, D. C., Vol. 2, 1962, pp. 849–853.
7. Lea, F. M., *Can. J. of Res.* **27**:297 (1949).

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Corrosion Control; Pipe.