ACID ATTACK IN A VITRIFIED CLAY PIPE (VCP) SEWER LINE – A PETROGRAPHIC AND CHEMICAL INVESTIGATION

ABSTRACT

Tempered addition of wollastonite (calcium metasilicate, $CaSiO_3$) in a clay pipe is not uncommon, as in many other ceramic products. Fluxing properties, freedom from volatile constituents, whiteness, and acicular properties of wollastonite provide various benefits in the ceramics, e.g., decreased shrinkage and gas evolution during firing, increased green and fired strength, maintain brightness during firing, permits fast firing, reduces crazing, cracking, and glaze defects, contributes calcium oxide to glaze formation without outgassing, provides higher impact strength from acicular structure, reduces thermal expansion, etc. In nature, wollastonite occurs in thermally metamorphosed impure limestones by high temperature reactions of calcite ($CaCO_3$) and quartz (SiO_2) in the limestone as $CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2$.

Wollastonite, however, may become unstable in an acidic environment, such as inside a sewer pipe. Oxidation of typical hydrogen sulfide gas in a sewer by sulfur-oxidizing bacteria (e.g., *thiobacillus*) generates sulfuric acid (H_2SO_4), which usually reacts with ‘concrete’ sewer pipes, and corrodes calcium-bearing pastes and aggregates from concrete as chemical erosion (acid attacks) of concrete pipe. Vitrified Clay Pipe (VCP), due to its usual lack of calcium-bearing phases, and its characteristic denser aluminosilicate composition is usually resistant to such sulfuric acid attacks.

Despite many known benefits in ceramics, tempered addition of wollastonite in a VCP, however, may provide that unwanted source of calcium in the pipe body to participate in a potentially deleterious chemical reaction with the sulfuric acid in the sewer environment. Wollastonite readily hydrolyses in an acid environment by $CaSiO_3 + 2H^+ \rightarrow Ca^{2+} + H_2SiO_3$ by an effective ion exchange reaction, where Ca^{2+} is exchanged with adsorbed H^+ and diffused out of the crystal structure into the solution, sometimes leaving a residual amorphous phase resembling the morphology of the parent wollastonite crystals (pseudomorphs).

The occurrence of gypsum ($CaSO_4 . 2H_2O$) in the reaction products of the wollastonite dissolution in a sulfuric acid environment is easily explained by precipitation of the Ca-saturated SO_4 solution. Most of the Ca^{2+} ions released from the wollastonite into solution reacted with the acid sulfate water through the following reaction:

$Ca^{2+} + SO_4^{2-} + 2H_2O \rightarrow CaSO_4 . 2H_2O$, or, in more complete form

$CaSiO_3 + H_2SO_4 \rightarrow CaSO_4 . 2H_2O + SiO_2 . nH_2O$

The products of reaction of wollastonite and sulfuric acid are, therefore, gypsum, and spherical (amorphous or colloidal) silica gel.

The present detailed microstructural and microchemical study of a distressed VCP is the authors' humble contribution to the first known such occurrence of distress in a VCP literature, due to potentially deleterious chemical reactions between the tempered wollastonite additives in the clay pipe with the sulfuric acid in the sewer environment that has generated gypsum and amorphous silica gel along the inside surface of the pipe, potentially causing spalling and cracking of the VCP along the inside surface, i.e. the surface that was in direct contact with the acidic environment of the sewer. Formation of gypsum from wollastonite itself is an expansive reaction, which, if occurs in a confined space within the VCP body can generate stresses leading to cracking of VCP. Furthermore, the amorphous silica gel, often occurring as spherical masses on the spalled inside surface along with gypsum can accommodate large amounts of water to cause further expansion.

Spectacular development of gypsum crystals, sometimes pseudomorphed after the long slender prismatic morphologies of wollastonite, sometimes associated with wollastonite maintaining its long prismatic morphology, sometimes coated on the surface of a reacted wollastonite crystal, sometimes associated with globular masses of silica gel, or, sometimes simply intermixed with gypsum, and silica gel are noticed *on the distressed (spalled) inside surfaces* of two of three samples, reportedly retrieved from failed locations of the pipe. Such reaction products are commonly known as *efflorescence deposits,* and they characteristically have small white spotted or pitted powdery to semi-crystalline masses all over the spalled inside surfaces.

Due to the direct association of gypsum on the distressed (spalled) inside surfaces of VCP samples, and, its association with tempered wollastonite additives, deleterious gypsum formation from sulfuric acid attack of the found tempered wollastonite, which, in turn, is the most likely candidate as the main source of the calcium found in the VCP samples is, therefore, judged to be the likely cause of the observed distress mechanism (spalling and cracking) of the inside surfaces of the pipe, which may eventually lead to pipe failure if spalling continues to threaten the thickness/thinness and hence load-bearing capacity of the VCP.

A comparative study with a companion sample from a separate and relatively older 15-in. diameter VCP line (in the vicinity of the distressed 33-in. line exposed to similar sewer environment and, reportedly, installed by the same manufacturer) show no apparent distress, which is linked to the absence of any calcium additive in this sound pipe for reaction with the sewer sulfuric acid, emphasizing the importance of careful control of the original VCP composition in a sewer environment.

INTRODUCTION

The most common type of distress in a portland cement concrete sewer pipe is by sulfuric acid generated within the pipe by oxidation of hydrogen sulfide gas in the moist sewer environment by the sulfur-oxidizing bacteria [1]. Sulfuric acid attacks calcium components in the concrete, and, causes chemical erosion of the inner liner of the pipe, preferential dissolution of cement paste and calcareous aggregates relative to siliceous aggregates in concrete, along with expansive formations of gypsum, ettringite/thaumasite phases [1].

Unlike concrete sewer pipe, however, due to the absence of calcium-bearing phases and characteristic dense aluminosilicate composition, vitrified clay pipe (VCP) is usually resistant to sulfuric acid attacks. Keeping the VCP free of any calcium-bearing phases during manufacturing is, therefore, important in a sewer environment to prevent any potentially deleterious chemical reactions between the calcium-phases and the sulfuric acid. Only hydrofluoric acid and highly concentrated caustic wastes are known to attack VCP [2].

VCPs are typically manufactured from fire clay, shale, surface clay, or a combination of these materials, along with some tempered additives (to improve the performance and behavior of VCP during manufacturing process and service afterwards) [3]. ASTM C12-13 describes standard practice for installation of VCP [4]. Water absorption, quantity of acid-soluble materials, and resistance to crushing and hydrostatic forces are commonly tested in a VCP prior to installation [5], whereas, non-destructive techniques such as CCTV, laser, and pipe penetrating radar (PPR) i.e. underground in-pipe application of ground penetrating radar (GPR) are used for detection of residual VCP thicknesses, defects, cavities, etc. during failure investigation of VCP in the field [6].

THE DISTRESSED 33-IN. VCP OF THIS STUDY

The following map in Figure 1 highlights the subject six to seven year old 33-in. diameter vitrified clay sewer pipe of No. 53 trunk sewer in Palm Desert and Rancho Mirage, California that is experiencing internal spalling of the pipe wall surface, essentially along its entire length of 18,575 liner feet - to the point of collapse and other failures at several locations. CCTV survey of most of the sewer and PPR survey of almost half-length of the entire sewer line detected spalling and loss of wall thicknesses to the extent of as much as 1.5-in. (of the nominal 3.5-in. thickness of the original VCP wall).

The entire VCP line in the map (marked in various colors for the purpose of investigation) is extended from Manhole Nos. 1 through 52. CCTV and PPR survey were done by SewerVUE crew along the portion in between Manhole Nos. 8 and 50, which represents approximately 9580 liner feet of the line. PPR survey determined variation in pipe wall thicknesses from as low as 2.44-in. at areas of spalling to as much as 3.87-in. in the relatively sound locations, i.e. approximately 1.5-in. loss of pipe wall thickness from spalling of the interior surface of the wall.

A total of three saw-cut samples of this distressed VCP approximately 105 to 162 sq. in. in lateral dimensions were received for this study from locations between two the Manholes identified as MH5 and MH9. The first sample (identified as Sample# 001, Lab# 001) has a sound exterior and partially spalled interior surface (having visible cracks near the interior surface oriented parallel to the interior surface), approximately 2½ in. in nominal thickness, and is from the reach between MH5 and MH6. The second sample (identified as Sample#001, Lab# 002) has a sound exterior and sound interior surface, approximately 3¼ in. in nominal thickness, and is from the reach between MH7 and 7A. The third sample (identified as Sample# 002, Lab# 1) has a sound exterior and completely spalled interior surface, approximately 2½ in. in nominal thickness, and is from the portion between MH7A and MH9. The three samples, therefore represent three different states of internal pipe wall surface conditions, from relatively sound pipe wall in the second sample to partially spalled wall in the first sample, to completely spalled wall in the third sample, having a ¾ in. loss of the pipe wall thickness from the relatively sound to the spalled samples.

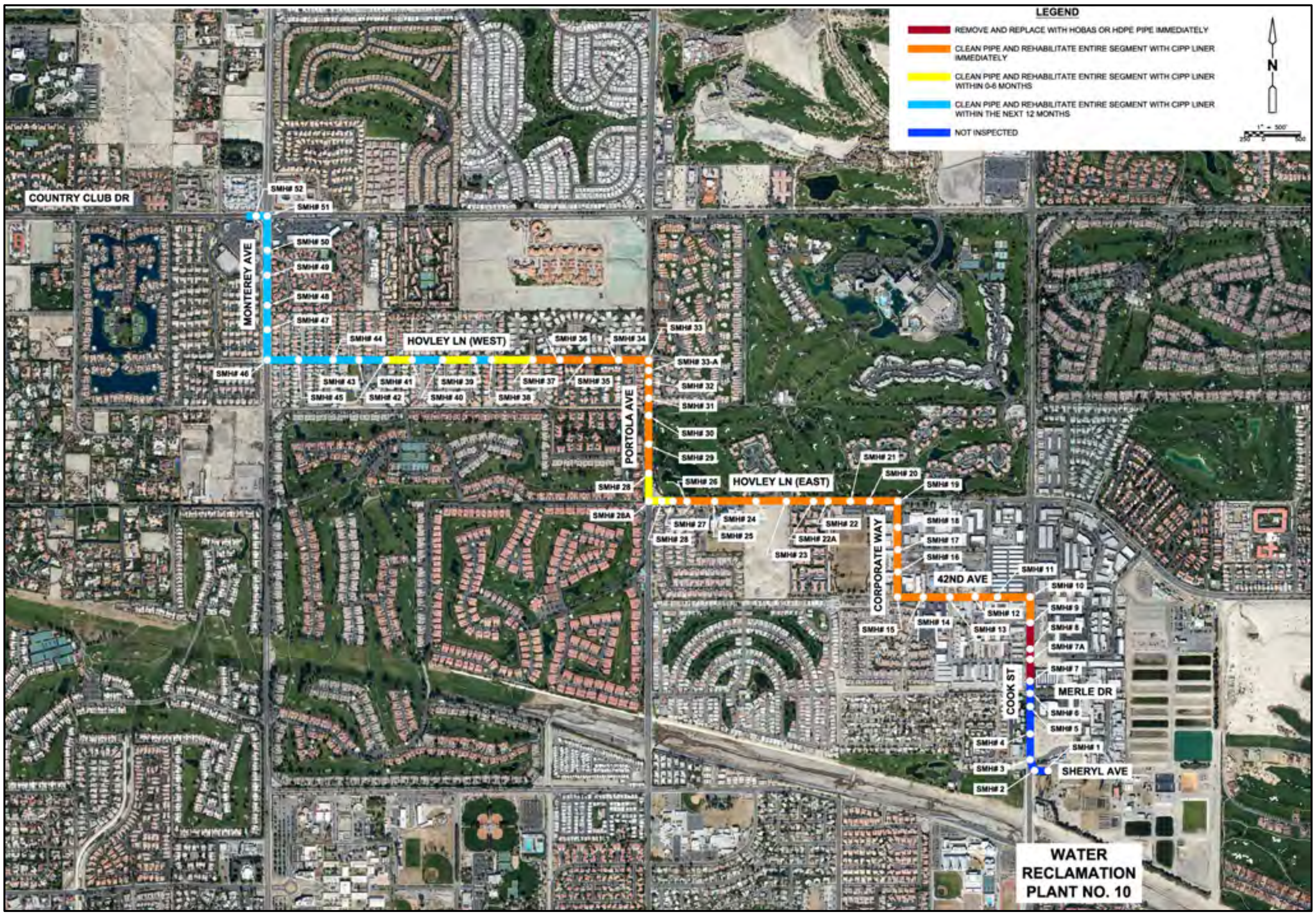


Figure 1: Vitrified clay sewer pipe in Palm Desert and Rancho Mirage, California.

AN OLDER SOUND 15-IN. VCP IN THE VICINITY FOR COMPARISON

A forth saw-cut sample from another apparently sound 15-in. diameter VCP, located around MH3 and MH4 of the existing 33-in. line (oriented parallel to the distressed 33-in. line and connects to it at MH3) is studied for comparison with the three samples of the 33-in. line. This forth sample has a sound exterior surface, and a sound interior surface having a thin dark gray film of dried sewer sludge, and is 36 sq. in. in lateral dimension and 1½ in. in nominal thickness. This sound pipe is approximately 15 years older than the 33-in. distressed line, exposed to the similar sewer environment, and was, reportedly, manufactured by the same manufacturer.

Due to the apparently sound condition and longer years of service in the same sewer environment as the distressed pipe, a sample was taken from this sound, smaller diameter pipe to investigate if there is any major compositional difference between these two pipelines in the same sewer environment that may have played a role in explaining selective distress only in the recent line but not in the older one.

THE VCP SAMPLES FROM 33-IN. AND 15-IN. LINES

The following series of photos in Figures 2 and 3 show (clockwise within each set for each sample): the sound exterior surface conditions of all four samples, the variably spalled interior surface conditions of three samples from the 33-in. pipe and sound interior surface of the 15-in. pipe, and saw-cut cross sections of the samples showing the internal condition of the VCP body, as well as variations in thicknesses between the samples:

Figure 2: Conditions of VCP samples received.

The top two and the bottom left sets of photos are from the three samples of the distressed 33-in. VCP that show spalled interior walls of the pipe in the first and third samples with loss of cross sectional thicknesses, as well as visible cracks in the VCP body in the first sample oriented parallel to the interior wall.

The third set (from the first left after a clockwise rotation) is for the sample from the sound 15-in. pipe that is thinner than the 33-in. pipe and is compositionally different from the 33-in. pipe. This sound pipe sample shows a dark gray sound interior (sewer-side) surface having a thin film of dried sewer sludge, and sound exterior (soil-side) surface. The sample has an overall thickness of 2½ in., which represents the original thickness of the pipe wall (due to the absence of any spalling as in the distressed pipe).

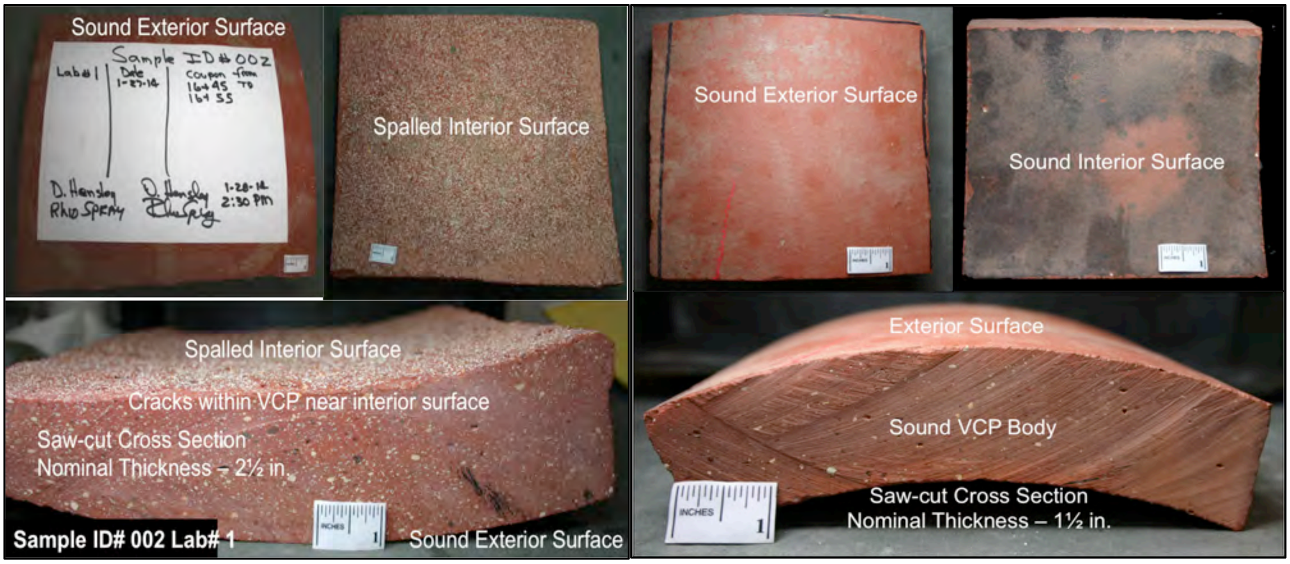


Figure 3: Conditions of VCP samples received.

PLASTIC AND NON-PLASTIC COMPONENTS OF VCP

The following photomicrographs of lapped cross section of three samples of the distressed 33-in. pipe in Figure 4 show various non-plastic components of VCP that are uniformly distributed over the reddish brown vitrified aluminosilicate clay matrix (plastic component) of the VCP.

Table 1 describes these components. The three main non-plastic components are: (a) clear, often short prismatic crystals of tempered addition of wollastonite (calcium metasilicate, $CaSiO_3$, some are circled), (b) light beige, subrounded argillaceous clay clots (ACCs), and (c) dark reddish brown previously fired grog particles (many with characteristic peripheral separations) and/or hematite-stained clay clots (HCCs).

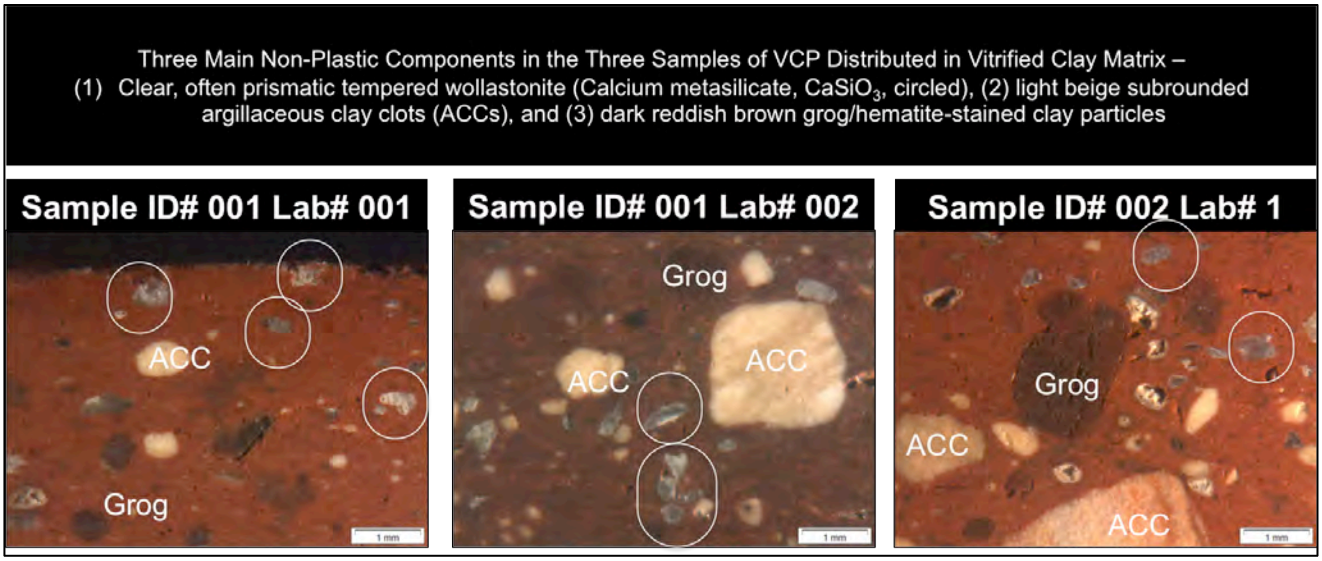

Three Main Non-Plastic Components in the Three Samples of VCP Distributed in Vitrified Clay Matrix – (1) Clear, often prismatic tempered wollastonite (Calcium metasilicate, $CaSiO_3$, circled), (2) light beige subrounded argillaceous clay clots (ACCs), and (3) dark reddish brown grog/hematite-stained clay particles

Figure 4: Non-Plastic components in VCP samples.

The following series of lapped cross section and blue dye-mixed epoxy-impregnated thin sections of VCP samples show these plastic and non-plastic components, as well as cracking and spalling of the VCP in the distressed pipe samples. In each set, the left and right columns show thin section photomicrographs, and the middle column shows lapped cross section (in the middle) and photomicrographs of lapped cross section of VCP from the top and bottom surface regions of the pipe (at the top and bottom rows in the middle column, respectively):

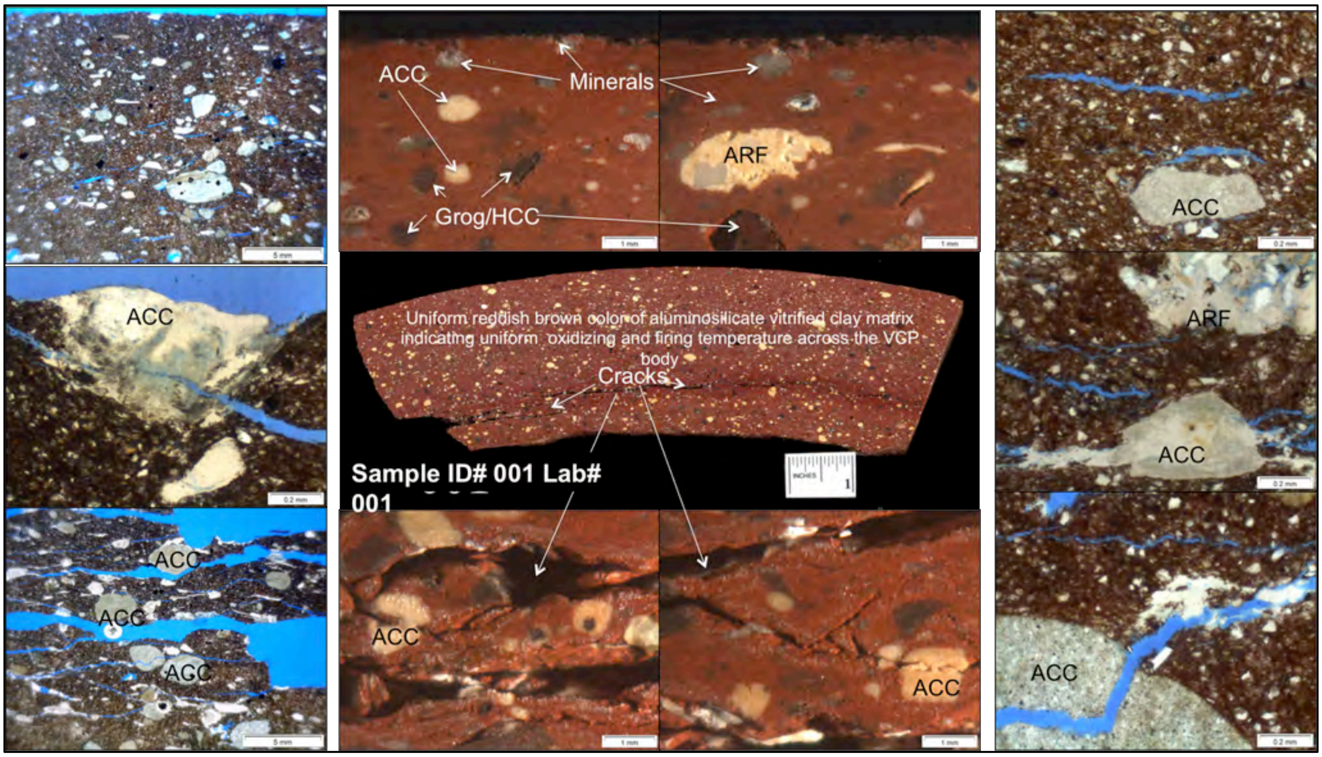


Figure 5: Lapped cross section and blue dye-mixed epoxy-impregnated thin section of VCP sample showing various plastic and non-plastic components, as well as cracking and spalling of the VCP. The left and right columns show thin section photomicrographs, and the middle column shows lapped cross section (in the middle) and photomicrographs of lapped cross section of VCP from the top and bottom surface regions of the pipe (at the top and bottom rows in the middle column, respectively).

For the three samples of distressed 33-in. pipe, lapped cross sections and thin sections show:

a) Colorless to off white short prismatic crystals of tempered wollastonite having nominal sizes of 0.4 mm along the long prism axes;

b) Light beige subangular to round, nominal 3 mm size argillaceous clay clots (ACCs) uniformly distributed throughout the VCP bodies;

c) Previously fired darker reddish brown grog particles and similar sized and colored hematite-stained clay clots that are relatively less abundant but uniformly distributed, and smaller in nominal sizes (1 mm); and

d) Also present at finer size and uniformly distributed over the vitrified matrix are fine angular grains of quartz (0.2 mm nominal size).

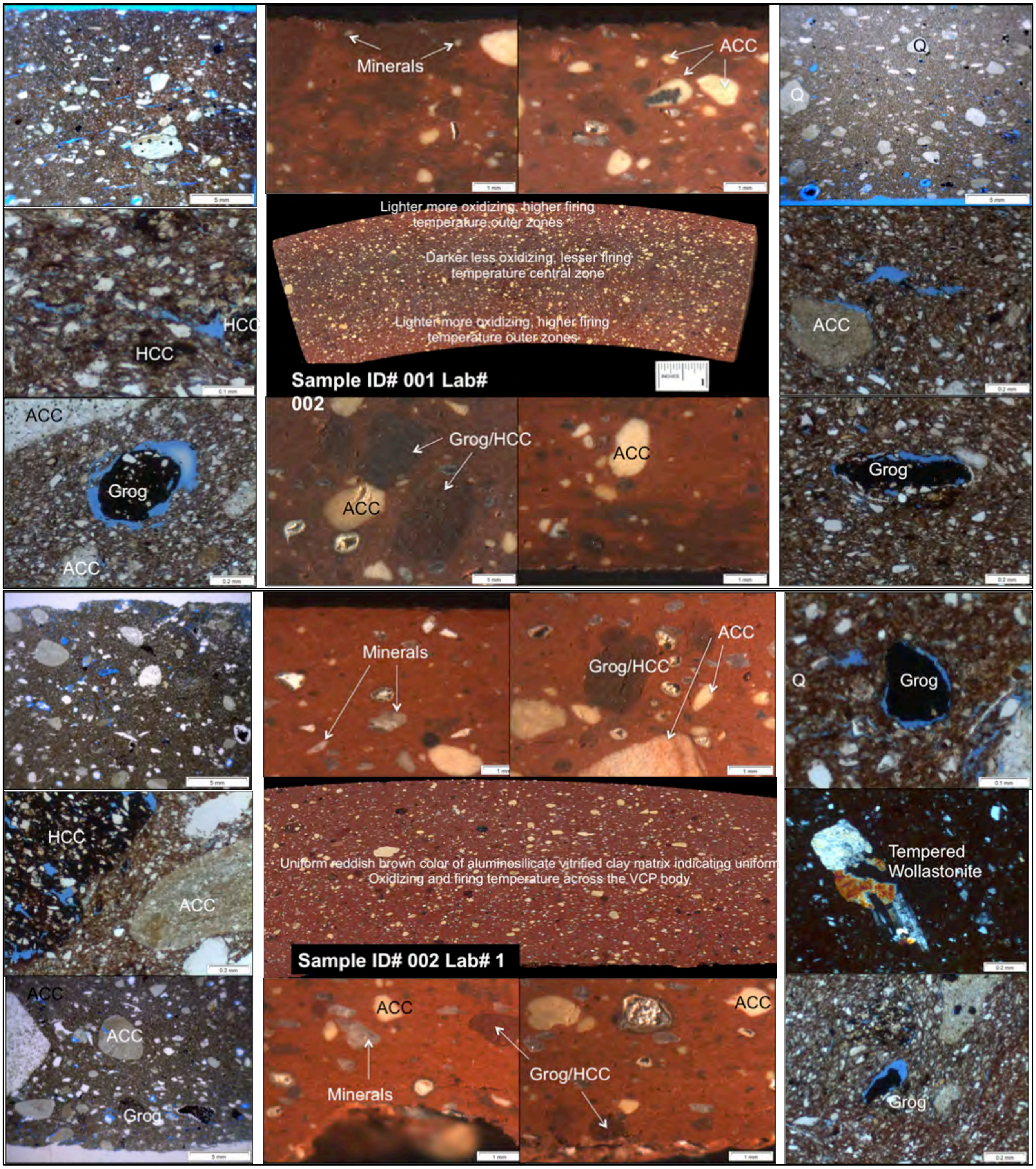


Figure 6: Lapped cross sections and blue dye-mixed epoxy-impregnated thin sections of VCP samples showing various plastic and non-plastic components. The left and right columns show thin section photomicrographs, and the middle column shows lapped cross section (in the middle) and photomicrographs of lapped cross section of VCP from the top and bottom surface regions of the pipe (at the top and bottom rows in the middle column, respectively).

The forth sample from the sound 15-in. pipe shows the following microstructural details:

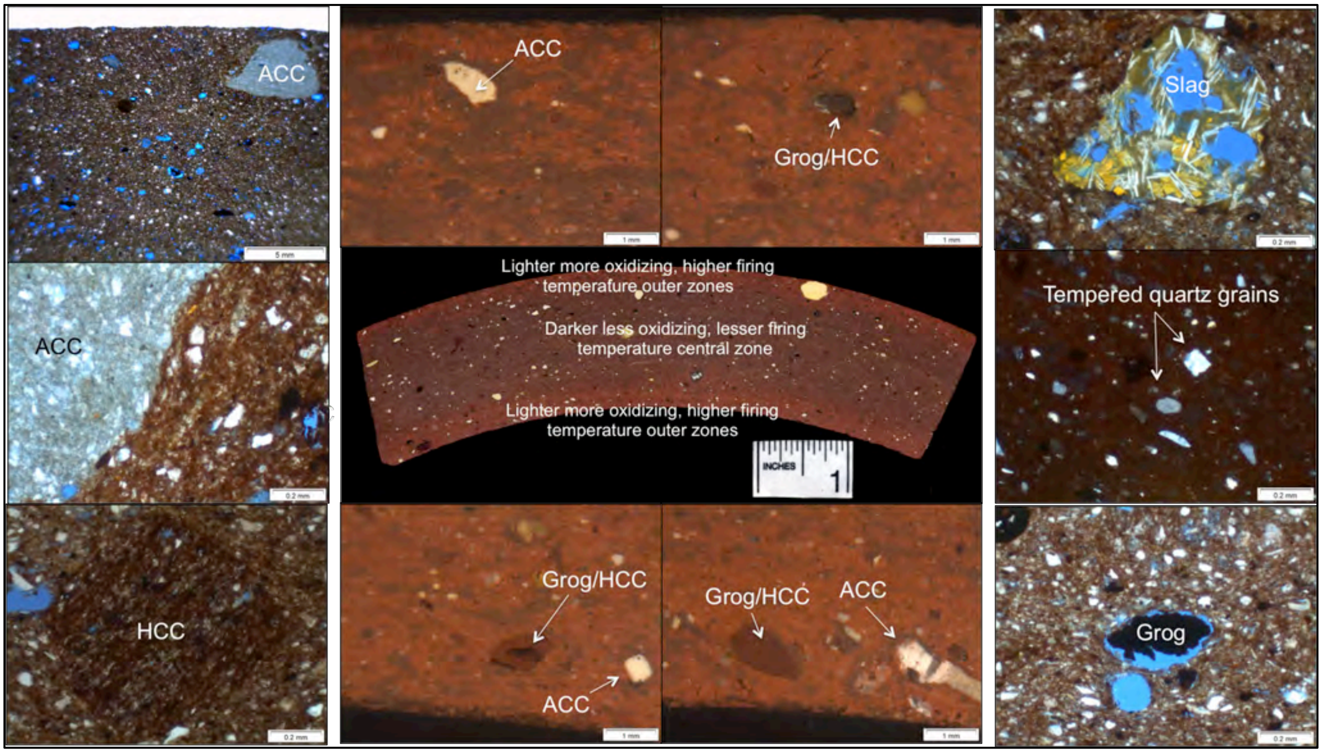


Figure 7: Lapped cross section and blue dye-mixed epoxy-impregnated thin section of sound VCP sample from 15-in. pipe showing various plastic and non-plastic components.

Binary images of distribution of argillaceous clay clots in Figure 8 show clear abundance of these particles in the distressed 33-in. pipe, as opposed to the sound 15-in. pipe.

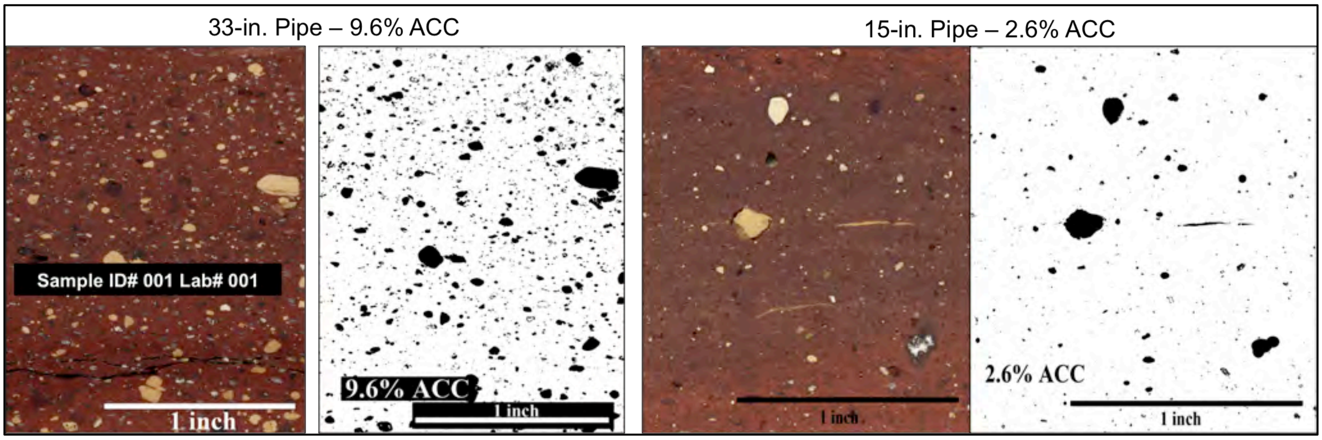


Figure 8: Binary images of distribution of argillaceous clay clots show clear abundance of these particles in the distressed 33-in. pipe, as opposed to the sound 15-in. pipe.

The following thin section photomicrographs of the sample from the sound 15-in. pipe in Figure 9 show many of these common non-plastic additives of 33-in. pipe, except wollastonite, and the presence of slag particles, all of which are also described in Table 2:

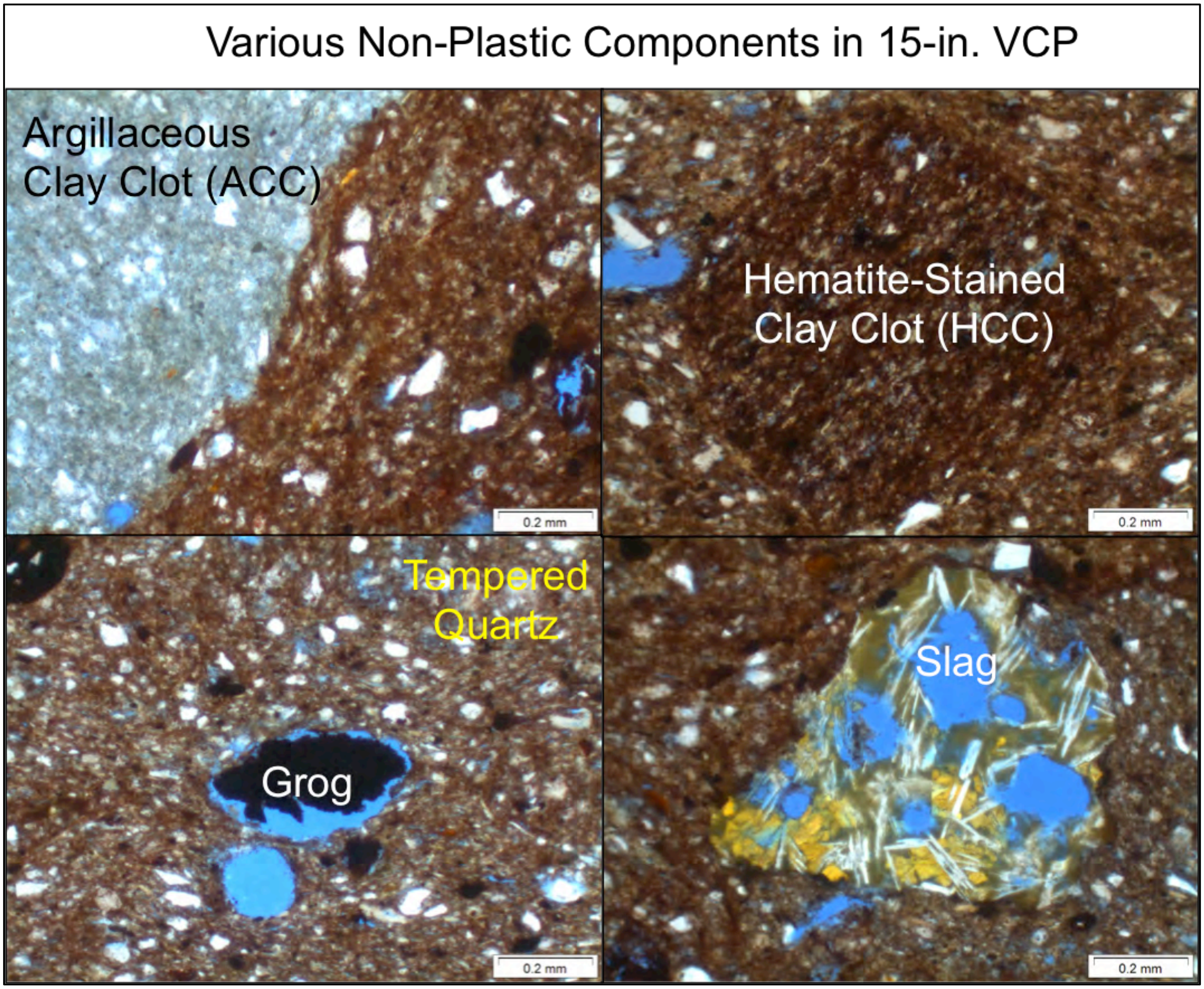


Figure 9: Thin section photomicrographs of the sample from the sound 15-in. pipe showing many non-plastic additives of 33-in. pipe, except wollastonite, and the presence of slag particles.

The major difference from the 33-in. distressed pipe samples are in: (a) far lesser abundance of argillaceous clay clots (ACCs) in the 15-in. sample (estimated to be 2.6 percent by volume), compared to as high as 9.6 percent by volume in the 33-in. pipe samples; and (b) absence of tempered wollastonite addition in the older 15-in. pipe, which is prevalent and uniformly distributed throughout the bodies of the 33-in. pipe samples.

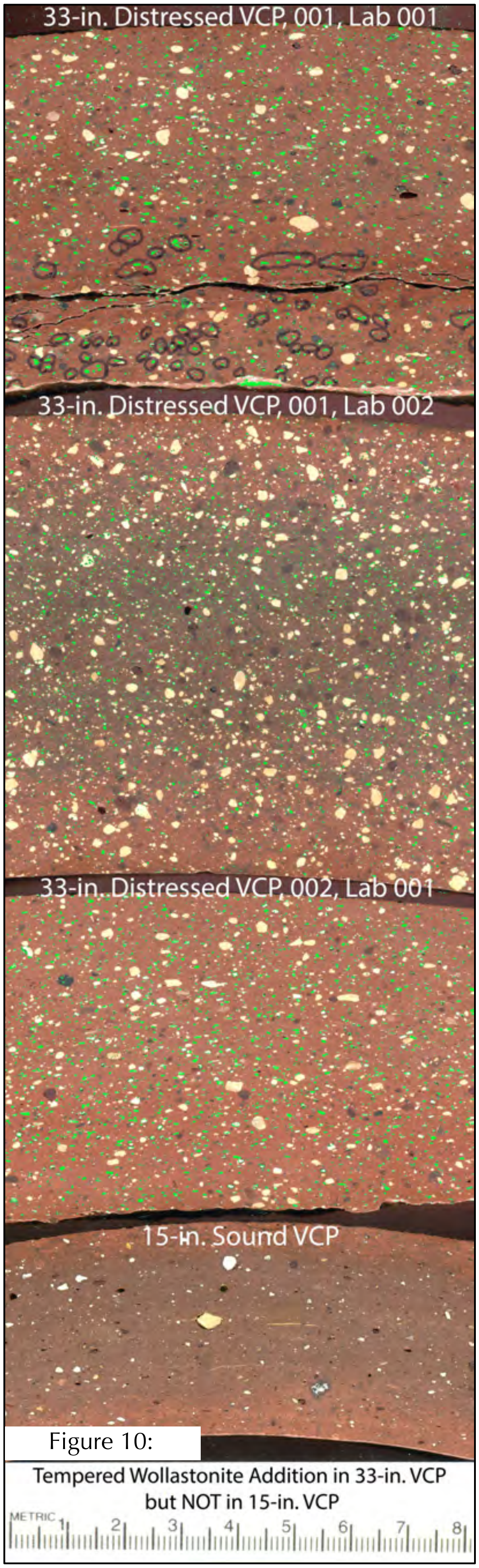


Figure 10:

Tempered Wollastonite Addition in 33-in. VCP but NOT in 15-in. VCP

Comparison of the lapped cross sections of three 33-in. distressed pipe samples with the 15-in. sound VCP at left clearly shows the *absence of wollastonite addition in the older 15-in. pipe, as opposed to numerous tempered wollastonite crystals (highlighted in green) in the 33-in. pipe samples*. Overall grain-sizes of wollastonite additives are smaller than ACCs and are short prismatic in shape (up to 0.4 mm in long prism lengths) as opposed to mostly equidimensional to some elongated subangular to well-rounded in shape for ACCs (mostly 3 mm in nominal size).

Also present are previously fired darker reddish brown grog particles, nominally 1 mm in size, many with characteristic separation from the lesser reddish brown vitrified matrix (separate formed during cooling of the pipe), and darker reddish brown hematite-stained clay clots (nominal 1 mm in size), both of which are present at far lesser abundance than the two major additives – wollastonite and ACCs.

All four samples contain numerous very fine angular tempered quartz crystals (0.2 mm in nominal size) uniformly distributed throughout the reddish brown aluminosilicate vitrified matrix of the pipes.

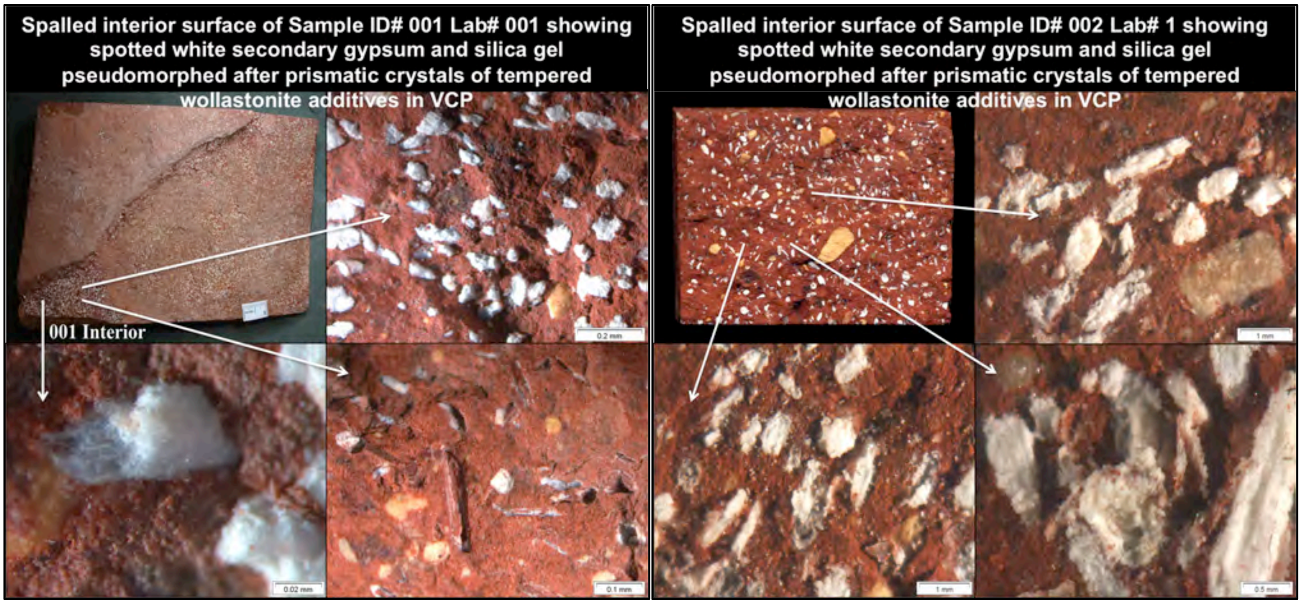
TYPES OF DISTRESS IN 33-IN. VCP SAMPLES

Two types of distresses are found in the samples from the failed 33-in. pipe:

1. Layer-by-layer spalling of VCP along the cracks oriented parallel to the interior sewer-side surfaces (like exfoliation) in two out of three samples. Spalling has caused loss of cross sectional thickness of the 33-in. pipe to as much as ¾ in. from the apparently sound sample to the two distressed samples of 33-in. pipe, as received. Two spalled samples are 2½ in. in nominal thicknesses, as opposed to 3¼ in. nominal thickness in the relatively sound sample of 33-in. pipe. This thickness reduction is consistent with the field study (PPR survey) where as much as 1½ in. reduction in pipe wall thickness from spalling was noticed across the entire surveyed length of the 33-in. line.

2. Cracking near the spalled interior surfaces in two out of three Samples – cracking within the body of VCP, mostly at the interior half is judged to be the reason for spalling of the internal wall and loss of cross sectional thickness of pipe.
3. In both distressed samples of 33-in. pipe it is only the interior (i.e. sewer-side) pipe wall surface that shows cracking and spalling – the exterior (i.e. soil-side) surfaces are free of any distress. Therefore, distress in three 33-in. line is determined to be due to loss of cross sectional thickness of pipe by spalling of the interior pipe wall surface under the influence of the sewer elements; the exterior soil is judged not contributed to the distress, at least in the samples examined.
4. Unlike concrete sewer pipe, where chemical erosion of portland cement paste by the sewer acid is common, causing different erosion of paste relative to siliceous aggregates, in the VCP body the distress is more due to physical action of spalling along cracks that were originally formed by deleterious chemical reactions of calcium minerals in the VCP with the sewer sulfuric acid. The overall aluminosilicate vitrified clay matrix is apparently unaffected by the sewer acid; it is the calcium minerals distributed throughout the vitrified clay matrix that have caused the cracking and spalling by expansive formation of gypsum at the locations of these calcium minerals (tempered wollastonite).

The following photos in Figure 11 show conditions of the spalled interior pipe wall surfaces in the two distressed VCP samples of 33-in. pipe that were in direct contact with the sewer elements. The spalled surfaces show a typical pitted or spotted appearance of fractured and sometimes popped-out (often left with empty pseudomorphs of crystal depressions) milky white partially dissolved tempered wollastonite crystals, distributed all over the spalled interior surfaces in both samples, many often coated with secondary gypsum crystals and spherical silica gel masses on the exposed/spalled reacted surfaces of fractured wollastonite crystals:


Spalled interior surface of Sample ID# 001 Lab# 001 showing spotted white secondary gypsum and silica gel pseudomorphed after prismatic crystals of tempered wollastonite additives in VCP

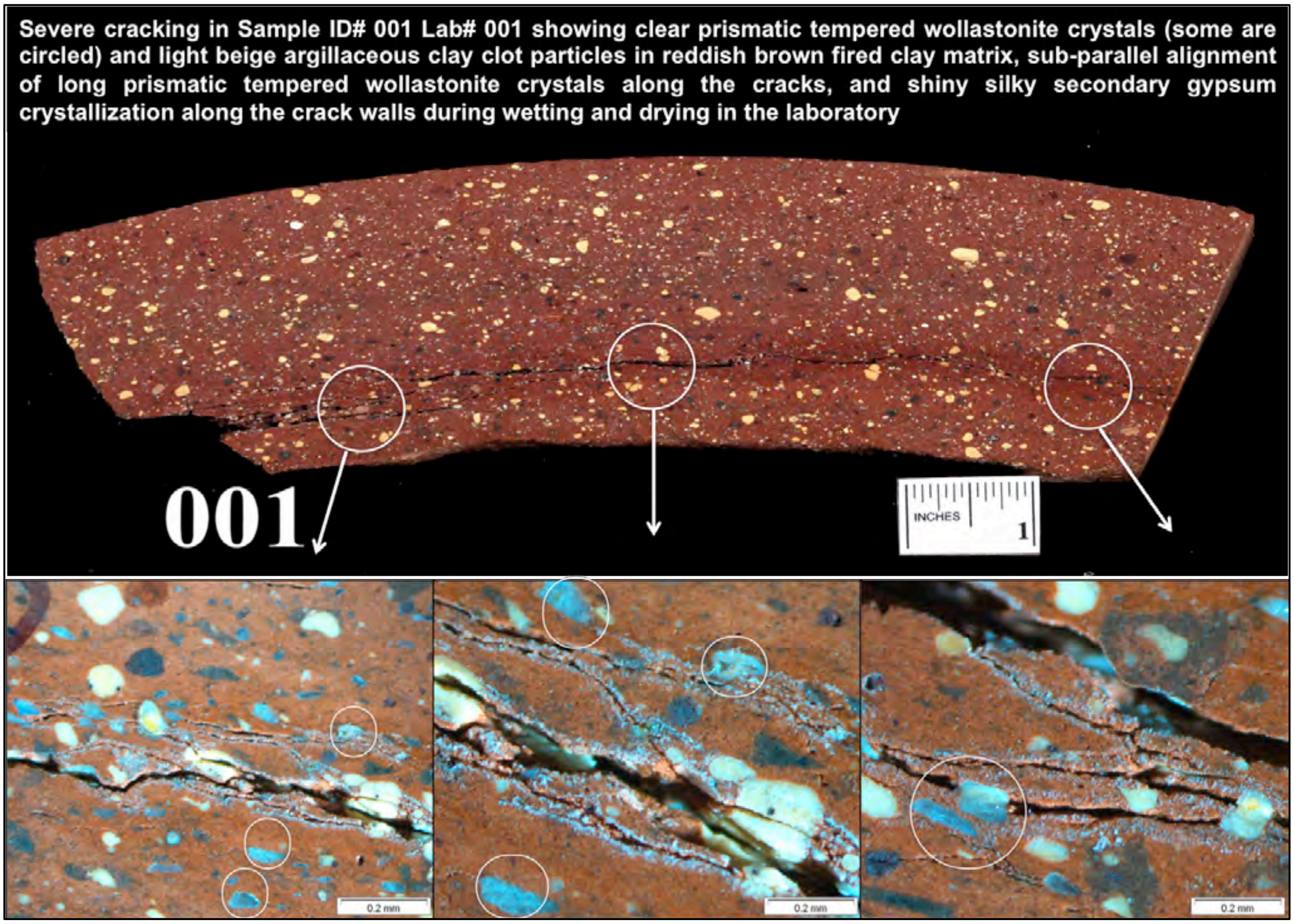
Spalled interior surface of Sample ID# 002 Lab# 1 showing spotted white secondary gypsum and silica gel pseudomorphed after prismatic crystals of tempered wollastonite additives in VCP

Figure 11: Conditions of the spalled interior pipe wall surfaces in the two distressed VCP samples of 33-in. pipe that were in direct contact with the sewer elements.

Cross-sections of the two distressed VCP samples from 33-in. pipe show visible cracks within the bottom half (i.e. interior sewer side) of the pipe, oriented parallel to the spalled interior wall surface. Spalling of the interior pipe wall surfaces, therefore, are judged to be due to the presence of these internal cracks in the VCP. Besides the inherent tempered wollastonite calcium minerals, there are no other sources of any calcium phase either inside the VCP body or around it (e.g., no mortar joints; pipe segments are reportedly joined by typical bell-and-spigot type joints in a VCP) are found that could contribute to the calcium ions for reaction with sewer acid.

A close examination of exposed and fractured tempered wollastonite crystals on the spalled surface of distressed 33-in. samples in a scanning electron microscope shows in situ formation of gypsum and silica gel on the surfaces of wollastonite.

The following lapped cross section photomicrographs show: (a) spectacular development of these cracks near the inside surface of VCP (at the inside half of pipe), (b) secondary gypsum crystallization along the cracks walls during wetting and drying of sample in the laboratory, (c) tempered wollastonite crystals in the VCP (some are circled in bottom row photos) and (d) light beige colored subrounded to rounded (larger in nominal sizes than wollastonite) particles of argillaceous clay clots (ACCs) – all uniformly distributed in the reddish brown aluminosilicate VCP body:



Severe cracking in Sample ID# 001 Lab# 001 showing clear prismatic tempered wollastonite crystals (some are circled) and light beige argillaceous clay clot particles in reddish brown fired clay matrix, sub-parallel alignment of long prismatic tempered wollastonite crystals along the cracks, and shiny silky secondary gypsum crystallization along the crack walls during wetting and drying in the laboratory

Figure 12: Cracking, secondary gypsum, tempered wollastonite, and ACCs in distressed pipe.

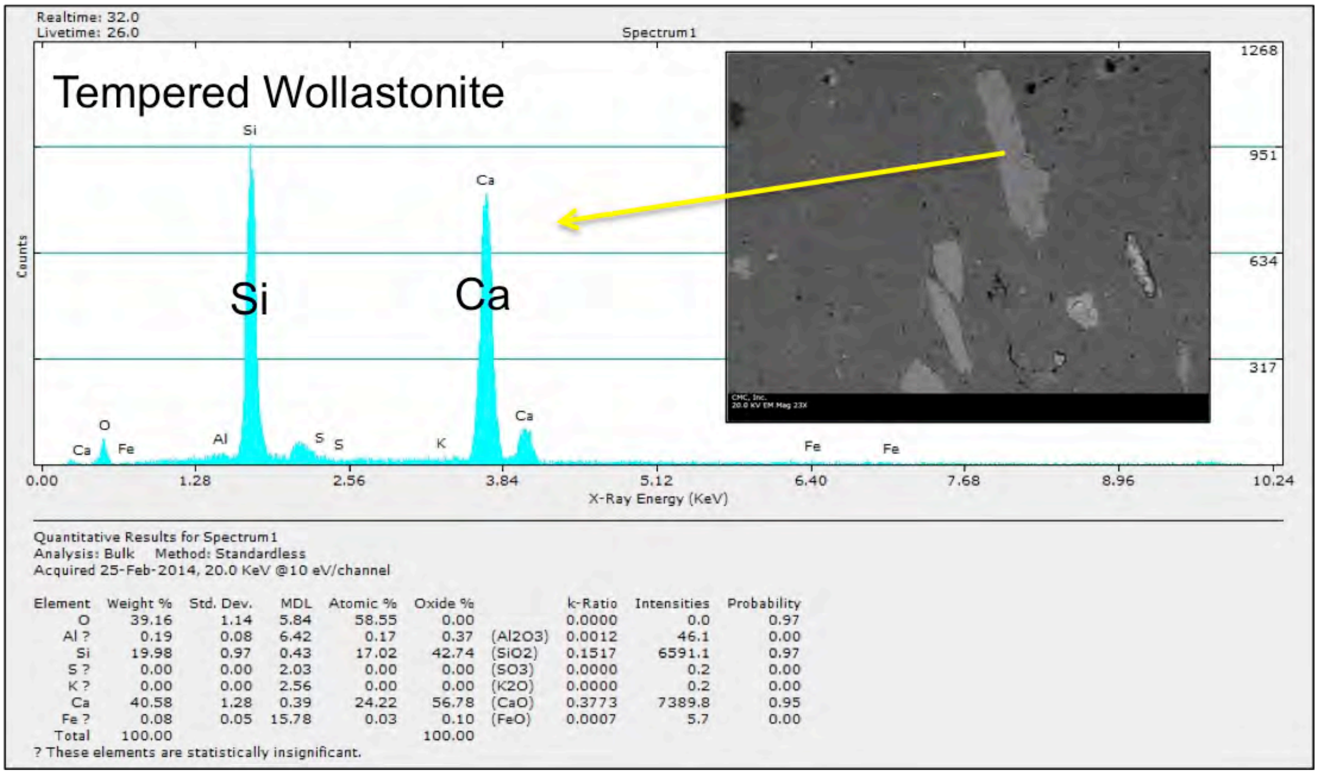
SCANNING ELECTRON MICROSCOPY AND ENERGY-DISPERSIVE X-RAY MICROANALYSIS (SEM-EDS) OF PLASTIC AND NON-PLASTIC COMPONENTS OF VCP

SEM-EDS studies of 33-in. VCP samples in a Cambridge (CamScan) Scanning Electron Microscope with an ancillary 4Pi elemental x-ray microanalyses determined:

(i) Long slender prismatic crystals of tempered wollastonite with characteristic calcium and silicon peaks, uniformly distributed with a faint alignment/parallelism of their long axes) as shown in Figure 13 where wollastonite crystals appear lighter gray against darker gray matrix, and,

(ii) Typical aluminosilicate (Al-Si, Si>Al in abundance) composition of the overall reddish brown vitrified clay matrix incorporating a minor amount of potassium and iron (iron oxide imparts the characteristic reddish brown stain of the vitrified clay body as shown in Figure 14 where matrix appeared darker gray than tempered wollastonite phase), (insets are backscatter electron images of the phases analyzed);

(iii) SEM-EDS studies directly on the spalled interior surfaces of 33-in. VCP in two spalled samples in Figures 15 and 16 show dissolution of tempered wollastonite and precipitation of secondary gypsum (Figure 15), and, spherical masses of amorphous (colloidal) silica gel (Figure 16):



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Quantitative Results for Spectrum1
Analysis: Bulk    Method: Standardless
Acquired 25-Feb-2014, 20.0 KeV @10 eV/channel

Element  Weight %  Std. Dev.    MDL  Atomic %  Oxide %           k-Ratio  Intensities  Probability
     O     39.16       1.14    5.84     58.55     0.00            0.0000          0.0         0.97
  Al ?      0.19       0.08    6.42      0.17     0.37  (Al2O3)   0.0012         46.1         0.00
    Si     19.98       0.97    0.43     17.02    42.74  (SiO2)    0.1517       6591.1         0.97
   S ?      0.00       0.00    2.03      0.00     0.00  (SO3)     0.0000          0.2         0.00
   K ?      0.00       0.00    2.56      0.00     0.00  (K2O)     0.0000          0.2         0.00
    Ca     40.58       1.28    0.39     24.22    56.78  (CaO)     0.3773       7389.8         0.95
  Fe ?      0.08       0.05   15.78      0.03     0.10  (FeO)     0.0007          5.7         0.00
 Total    100.00                                100.00
? These elements are statistically insignificant.
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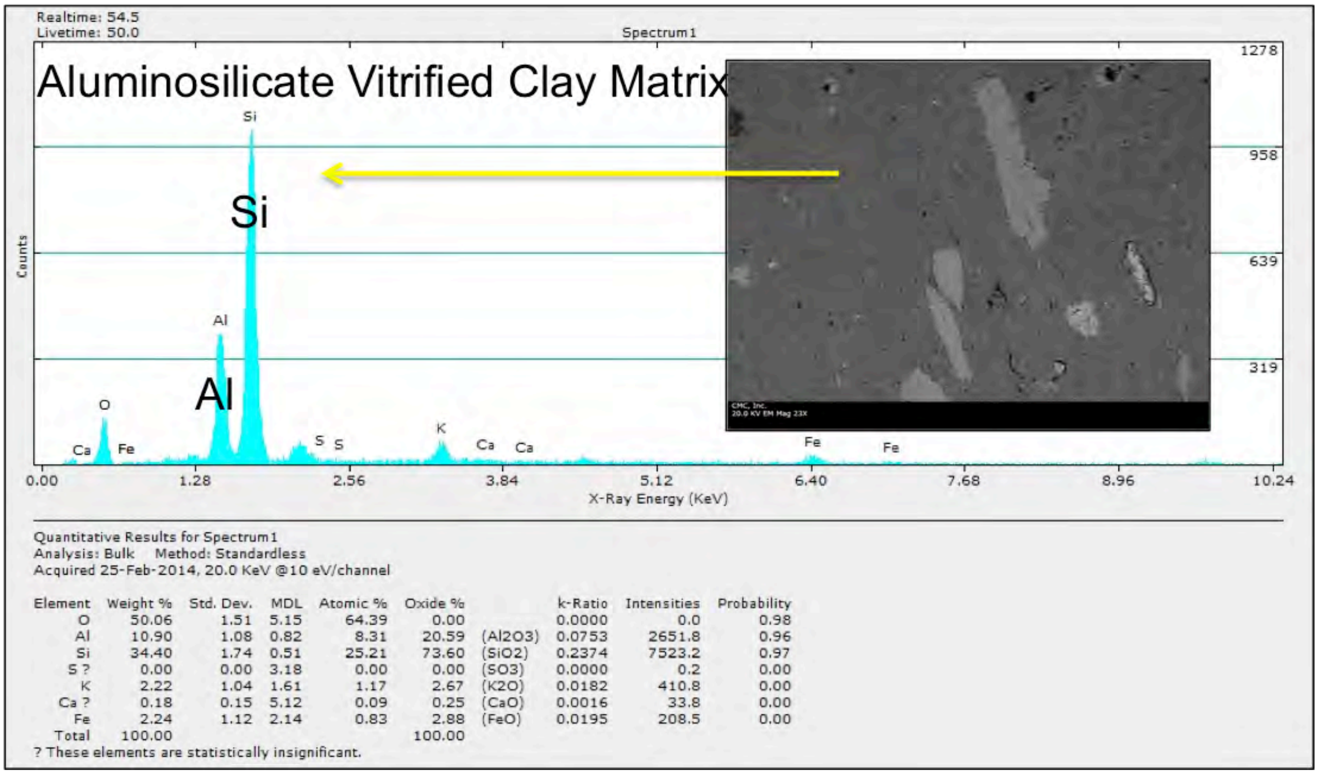
Figure 13: X-ray elemental analysis of long slender prismatic crystals of tempered wollastonite showing its characteristic calcium and silicon peaks. Inset shows backscatter electron image of an area in a distressed VCP from where compositional analysis of wollastonite crystals were done, where wollastonite appeared in brighter gray against darker gray vitrified matrix.

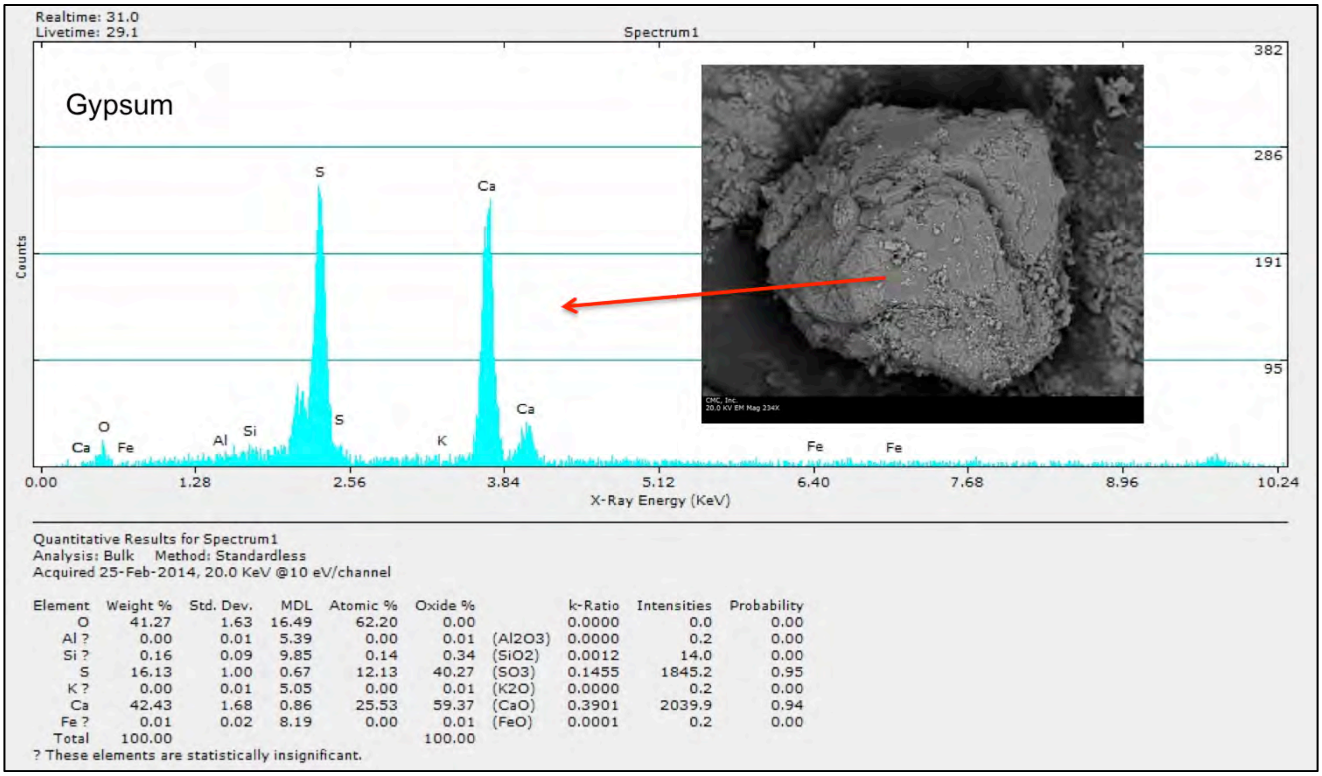


Quantitative Results for Spectrum1
Analysis: Bulk Method: Standardless
Acquired 25-Feb-2014, 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	MDL	Atomic %	Oxide %		k-Ratio	Intensities	Probability
O	50.06	1.51	5.15	64.39	0.00		0.0000	0.0	0.98
Al	10.90	1.08	0.82	8.31	20.59	(Al2O3)	0.0753	2651.8	0.96
Si	34.40	1.74	0.51	25.21	73.60	(SiO2)	0.2374	7523.2	0.97
S ?	0.00	0.00	3.18	0.00	0.00	(SO3)	0.0000	0.2	0.00
K	2.22	1.04	1.61	1.17	2.67	(K2O)	0.0182	410.8	0.00
Ca ?	0.18	0.15	5.12	0.09	0.25	(CaO)	0.0016	33.8	0.00
Fe	2.24	1.12	2.14	0.83	2.88	(FeO)	0.0195	208.5	0.00
Total	100.00				100.00				

? These elements are statistically insignificant.

Figure 14: X-ray elemental analysis of vitrified clay matrix showing its characteristic aluminum and silicon peaks. Inset shows backscatter electron image of an area in a distressed VCP from where compositional analysis of matrix is done, where tempered wollastonite grains appeared in brighter gray against darker gray vitrified matrix.

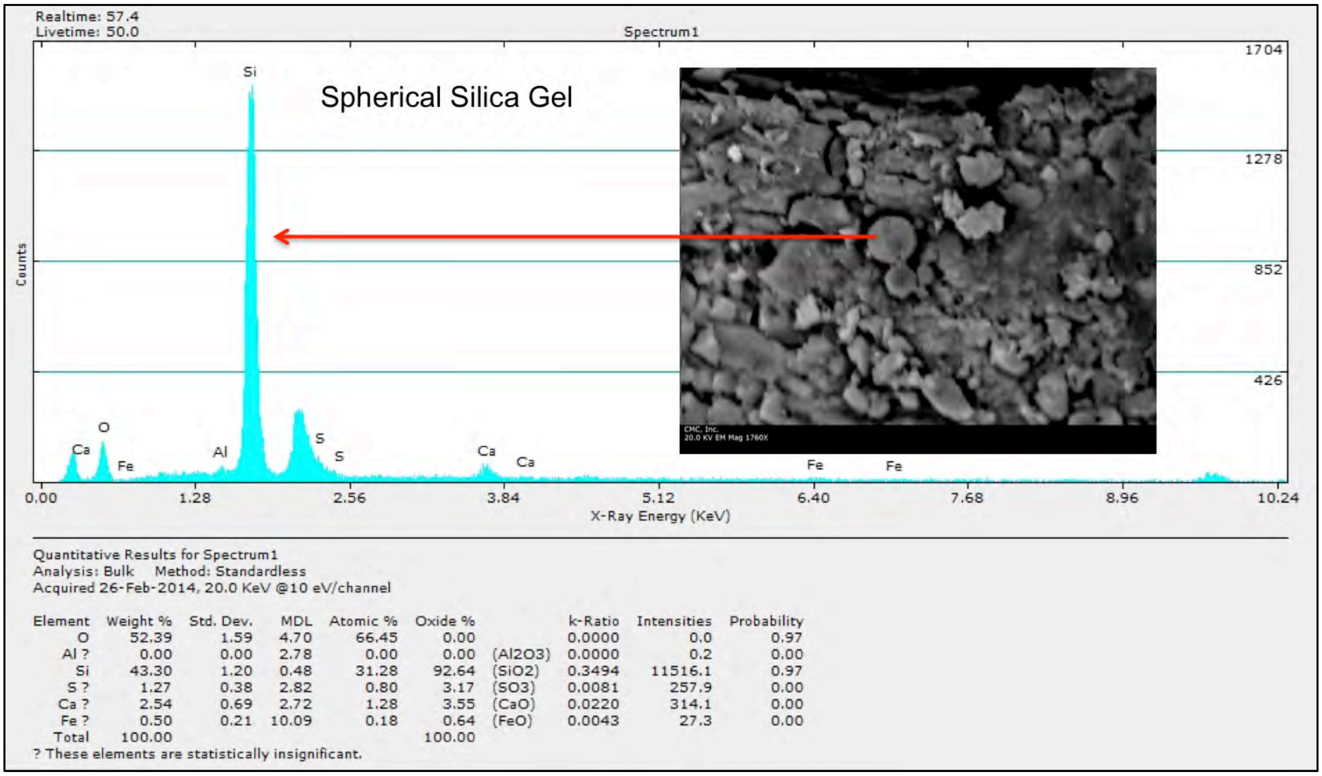


Quantitative Results for Spectrum1
Analysis: Bulk Method: Standardless
Acquired 25-Feb-2014, 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	MDL	Atomic %	Oxide %		k-Ratio	Intensities	Probability
O	41.27	1.63	16.49	62.20	0.00		0.0000	0.0	0.00
Al ?	0.00	0.01	5.39	0.00	0.01	(Al2O3)	0.0000	0.2	0.00
Si ?	0.16	0.09	9.85	0.14	0.34	(SiO2)	0.0012	14.0	0.00
S	16.13	1.00	0.67	12.13	40.27	(SO3)	0.1455	1845.2	0.95
K ?	0.00	0.01	5.05	0.00	0.01	(K2O)	0.0000	0.2	0.00
Ca	42.43	1.68	0.86	25.53	59.37	(CaO)	0.3901	2039.9	0.94
Fe ?	0.01	0.02	8.19	0.00	0.01	(FeO)	0.0001	0.2	0.00
Total	100.00				100.00				

? These elements are statistically insignificant.

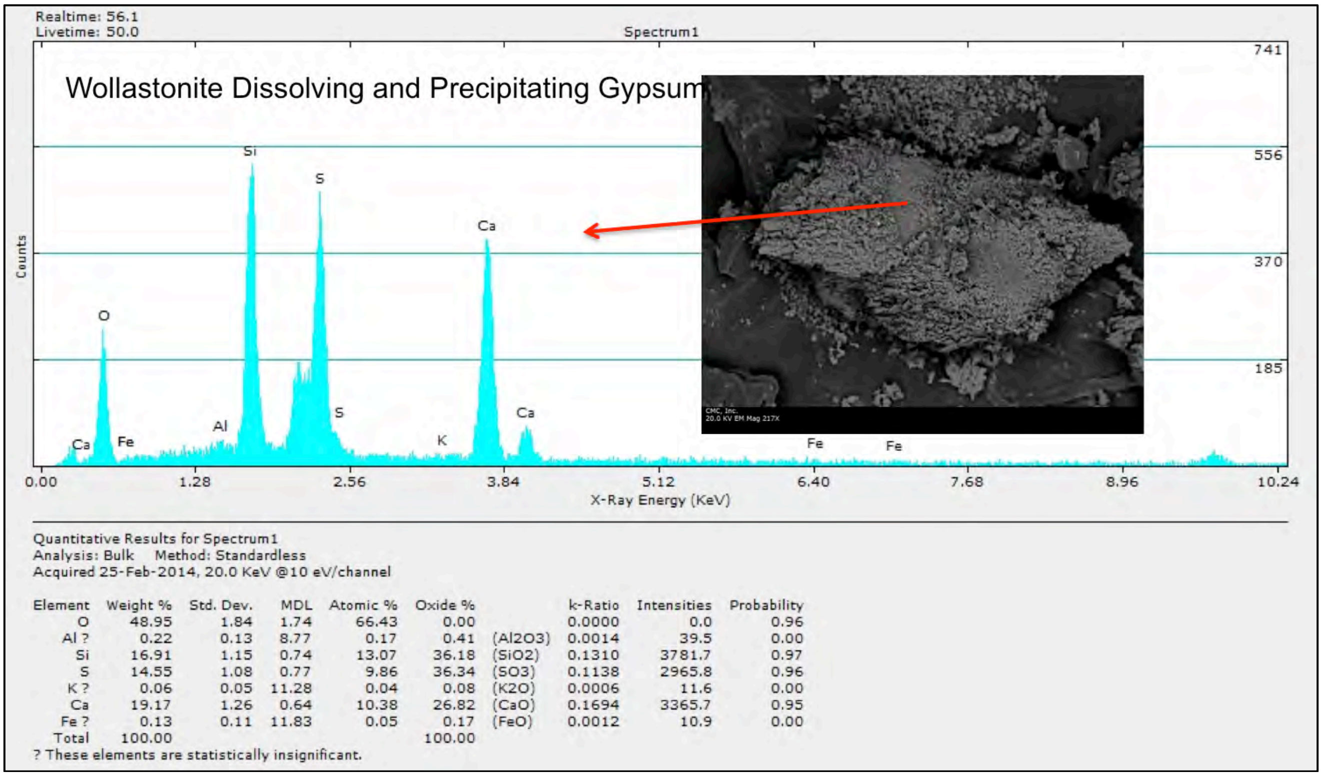
Figure 15: X-ray elemental analysis of secondary gypsum showing its characteristic calcium and sulfur peaks. Inset shows backscatter elector image of gypsum phase that was analyzed.



```
Quantitative Results for Spectrum1
Analysis: Bulk    Method: Standardless
Acquired 26-Feb-2014, 20.0 KeV @10 eV/channel

Element  Weight %  Std. Dev.    MDL  Atomic %  Oxide %            k-Ratio  Intensities  Probability
     O      52.39       1.59   4.70     66.45     0.00            0.0000          0.0         0.97
   Al ?      0.00       0.00   2.78      0.00     0.00  (Al2O3)   0.0000          0.2         0.00
    Si      43.30       1.20   0.48     31.28    92.64  (SiO2)    0.3494      11516.1         0.97
    S ?      1.27       0.38   2.82      0.80     3.17  (SO3)     0.0081        257.9         0.00
   Ca ?      2.54       0.69   2.72      1.28     3.55  (CaO)     0.0220        314.1         0.00
   Fe ?      0.50       0.21  10.09      0.18     0.64  (FeO)     0.0043         27.3         0.00
  Total    100.00                                100.00
? These elements are statistically insignificant.
```

Figure 16: X-ray elemental analysis of spherical masses of amorphous (colloidal) silica gel showing its characteristic calcium and sulfur peaks. Inset shows backscatter elector image of gypsum phase that was analyzed.



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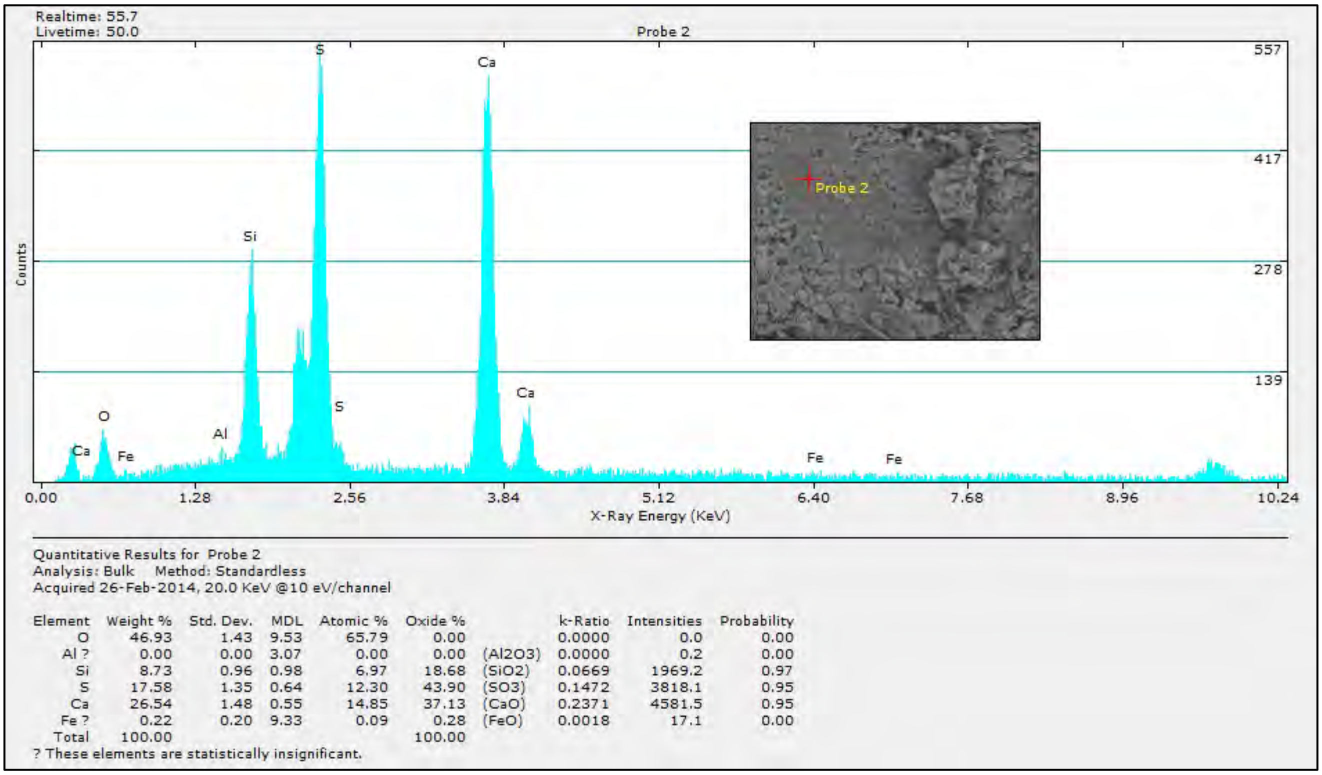
Quantitative Results for Spectrum1
Analysis: Bulk    Method: Standardless
Acquired 25-Feb-2014, 20.0 KeV @10 eV/channel

Element  Weight %  Std. Dev.    MDL  Atomic %  Oxide %            k-Ratio  Intensities  Probability
     O      48.95       1.84   1.74     66.43     0.00            0.0000          0.0         0.96
   Al ?      0.22       0.13   8.77      0.17     0.41  (Al2O3)   0.0014         39.5         0.00
    Si      16.91       1.15   0.74     13.07    36.18  (SiO2)    0.1310       3781.7         0.97
     S      14.55       1.08   0.77      9.86    36.34  (SO3)     0.1138       2965.8         0.96
    K ?      0.06       0.05  11.28      0.04     0.08  (K2O)     0.0006         11.6         0.00
    Ca      19.17       1.26   0.64     10.38    26.82  (CaO)     0.1694       3365.7         0.95
   Fe ?      0.13       0.11  11.83      0.05     0.17  (FeO)     0.0012         10.9         0.00
  Total    100.00                                100.00
? These elements are statistically insignificant.
```

Figure 17: X-ray elemental analysis of tempered wollastonite in 33-in. VCP's spalled internal pipe wall surface - dissolving and precipitating secondary gypsum on the surface of wollastonite. Inset shows backscatter elector image of gypsum phase that was analyzed.



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Quantitative Results for  Probe 2
Analysis: Bulk    Method: Standardless
Acquired 26-Feb-2014, 20.0 KeV @10 eV/channel

Element  Weight %  Std. Dev.  MDL   Atomic %  Oxide %           k-Ratio  Intensities  Probability
     O     46.93      1.43    9.53    65.79     0.00            0.0000        0.0         0.00
  Al ?      0.00      0.00    3.07     0.00     0.00  (Al2O3)   0.0000        0.2         0.00
    Si      8.73      0.96    0.98     6.97    18.68  (SiO2)    0.0669     1969.2         0.97
     S     17.58      1.35    0.64    12.30    43.90  (SO3)     0.1472     3818.1         0.95
    Ca     26.54      1.48    0.55    14.85    37.13  (CaO)     0.2371     4581.5         0.95
  Fe ?      0.22      0.20    9.33     0.09     0.28  (FeO)     0.0018       17.1         0.00
 Total    100.00                              100.00
? These elements are statistically insignificant.
```

Figure 18: X-ray elemental analysis of tempered wollastonite in 33-in. VCP's spalled internal pipe wall surface - dissolving and precipitating secondary gypsum on the surface of wollastonite. Inset shows backscatter elector image of gypsum phase that was analyzed.

Photomicrographs and x-ray microanalyses in Figures 17 and 18 further showed tempered wollastonite in 33-in. VCP's spalled internal pipe wall surface - dissolving and precipitating secondary gypsum on the surface of wollastonite:

X-RAY DIFFRACTION

X-ray diffraction analysis of pulverized portion of a thin skin of the spalled interior surface of a 33-in. VCP sample was carried out in a Siemens D 5000 powder diffractometer (ran with copper k-alpha radiation, at two degrees per minute scan, with theta-two theta geometry of goniometer).

The result shows spectacular secondary gypsum crystals along with tempered and original quartz grains. Gypsum peaks in the XRD is consistent with its observation in association with tempered wollastonite in the SEM-EDS analysis.

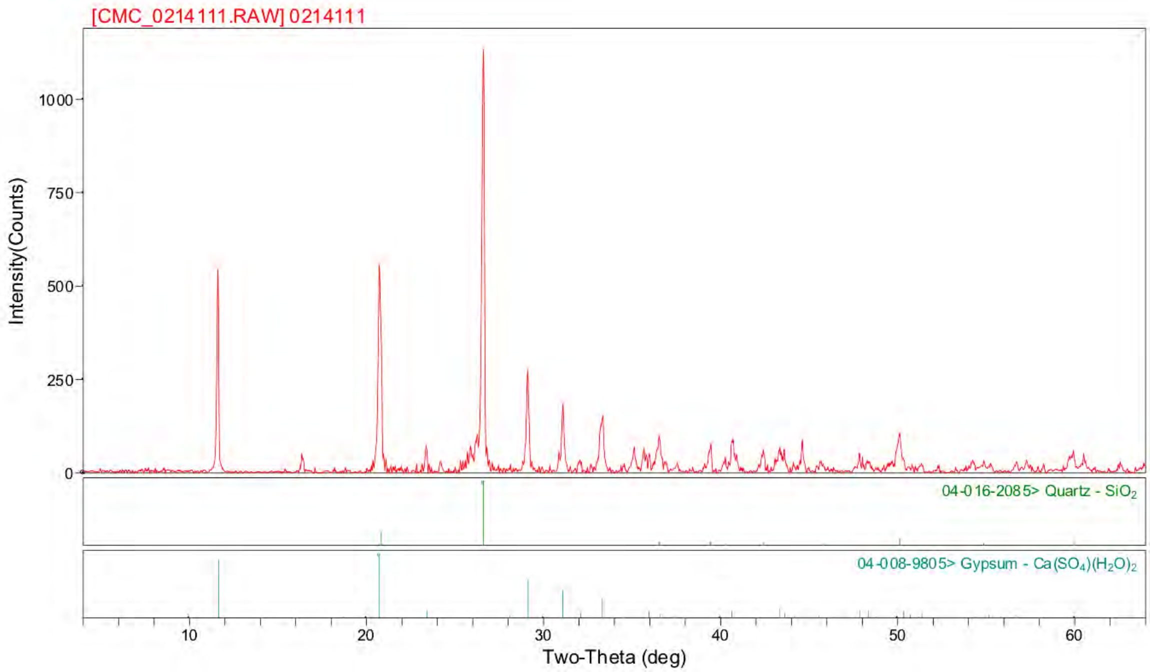


Figure 19: X-ray diffraction pattern of pulverized portion of a thin skin of the spalled interior surface of a 33-in. VCP.

MECHANISM OF DISTRESS OF VCP - SECONDARY GYPSUM CRYSTALLIZATION FROM SEWER GASES AND ACIDIC/SULFATE (SULFURIC ACID) EXPOSURES IN SEWER

The inner (i.e. sewer-side) surfaces of VCP in two distressed samples from 33-in. pipe show cracking, spalling, and loss of cross sectional thickness of VCP to at least $^3/_4$ in. - both of which indicates a potentially deleterious influence of the sewer elements in causing the pipe failure. The outer (i.e. soil-side) surfaces of all samples from both pipes are sound and formed - indicating a lack of any influence of soil elements in causing any distress in the VCP.

Cracking, subsequent spalling, and loss of pipe wall thickness along the interior (sewer-side) surface in the 33-in. pipe are all determined to be due the a deleterious chemical reaction between the tempered wollastonite phases in the 33-in. line with the sewer sulfuric acid resulting in secondary gypsum and silica gel formation – both of which are associated with significant expansions, and hence cracking and spalling of pipe to accommodate that expansion in a confined space in VCP.

Therefore, it is determined that the sewer elements, particularly the hydrogen sulfide gas in the sewer, and, corresponding sulfuric acid attacks from the sewer elements (in the influence of sulfur-oxidizing bacteria, e.g., thiobacillus, which colonizes in the moist film of interior pipe wall) have influenced the spalling and cracking of VCP along the inner (i.e. sewer-side) surface of the pipe than any influence of soil or its potentially deleterious components (e.g., sulfates) from the environment.

External sulfates from soil, if present, at least did not cause any characteristic distress (e.g., surface-parallel cracking, erosion, secondary gypsum crystallization along the outer soil-side surface, salt hydration distress, etc.) in the three samples of the 33-in. pipe examined. Formation of secondary gypsum and silica gel on and near the spalled interior surface in the distressed pipe are judged to have played more plausible roles in the VCP distress than any external influence of soil.

Scanning electron microstructural evidence of spalled interior surfaces of two distressed samples show: (a) dissolution of tempered wollastonite crystals, and (b) precipitation of secondary gypsum crystals and spherical masses of silica gel, both often associated with the dissolved wollastonite crystals, or, often as slender prismatic pseudomorphs of the tempered wollastonite crystals.

Such direct association of tempered wollastonite crystals with secondary gypsum and silica gel on the spalled interior surfaces of distressed pipe samples indicate that it is the source of calcium in these tempered wollastonite crystals (calcium metasilicate) that has participated in dissolution and precipitation of gypsum on the inside surfaces, often associated with cracking, spalling along inside surfaces, and loss of cross sectional thickness of VCP. Confined formation of secondary gypsum and silica gel at the expense of tempered wollastonite is judged to have caused stresses to develop cracking and spalling.

VCP, unlike concrete pipe, by nature is usually resistant to sulfuric acid attacks in a sewer environment, which is contributed to its usual lack of calcium phases in the composition. However, tempered wollastonite crystals can provide that source of calcium in a VCP, which, in the presence of sulfuric acid, can cause deleterious reactions by dissolution of wollastonite and expansive precipitation of secondary gypsum and amorphous silica gel.

The deterioration reaction is judged to be as follows:

$CaSiO_3$ (VCP's Wollastonite) + H_2SO_4 (Sewer's sulfuric acid) →

$CaSO_4.\ 2H_2O$ (Gypsum) + $SiO_2.\ nH_2O$ (Silica Gel)

Locations in the VCP having high concentrations of sulfuric acid and direct access to wollastonite crystals are more prone to VCP distress than elsewhere.

SEWER SULFURIC ACID EXPOSURE IN THE SOUND 15-IN. PIPE

As opposed to large-scale cracking and spalling of 33-in. to the point of reported collapse of pipe at various locations, similar exposures to sewer sulfuric acid, apparently for longer periods of time, however, did not cause any visible cracking or spalling or loss of cross sectional thickness of the 15-in. pipe sample.

Reasons for such lack of any major distress is judged to be due to apparent absence of any major calcium minerals in the 15-in. pipeline (as opposed to tempered wollastonite crystals in the 33-in. line) and hence lack of any deleterious reactions of a calcium mineral of VCP with the sewer sulfuric acid to cause expansive formation of gypsum.

Two common tempered additives, besides quartz grains, as mentioned before, are argillaceous clay clots (ACCs) but at significantly lower amounts than that found in the 33-in. VCP samples, and (b) grog, and hematite-stained particles. Another interesting additive is vesicular slag particles (nominal 1 mm size) that are compositionally similar to the overall aluminosilicate composition of the vitrified clay matrix, and hence have tight interfaces to the matrix (as opposed to the characteristic peripheral separations around grog particles). These slag particles are obvious better additives in VCP for performance in a sewer environment than any tempered calcium mineral additives.

On the interior wall surface of the 15-in. line is a very film dark gray film of dried sewer sludge that shows characteristic map cracking of the dried sludge for most of the internal wall surface, except only two locations (shown in the following photomicrographs of the interior surface in a 105 sq. in. area), apparently less than 0.5 mm in size where local micro-blistering and pop out-type localized loss are observed due to chemical reaction of minor amounts of calcite crystals in the original argillaceous clay clot masses and sewer sulfuric acid that caused localized formation gypsum within the clay clot masses from the fine, tiny calcite grains in the ACCs. None of these micro-blisters or popouts from localized gypsum formation from sewer sulfuric acid, however, caused any spalling of the VCP, or even of the sludge film let alone to cause any distress.

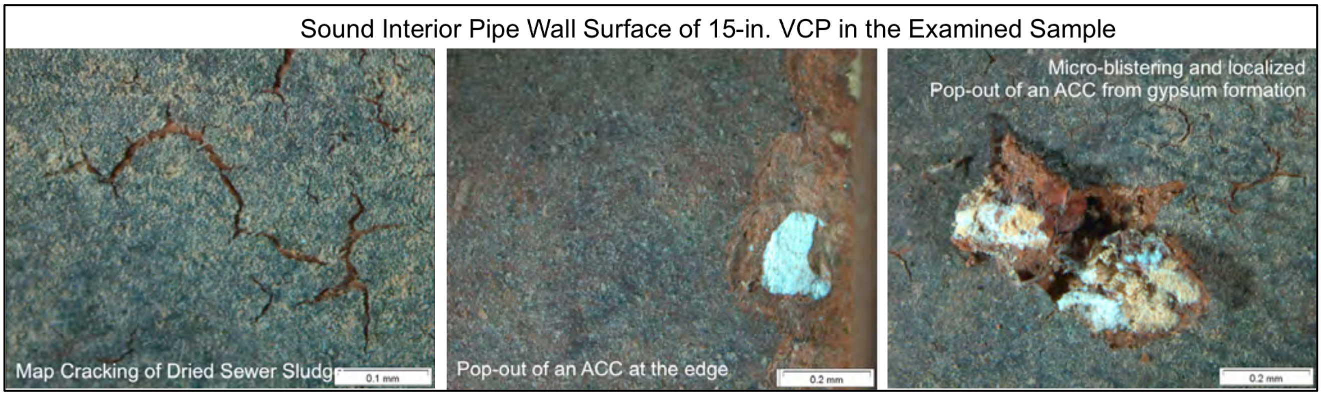
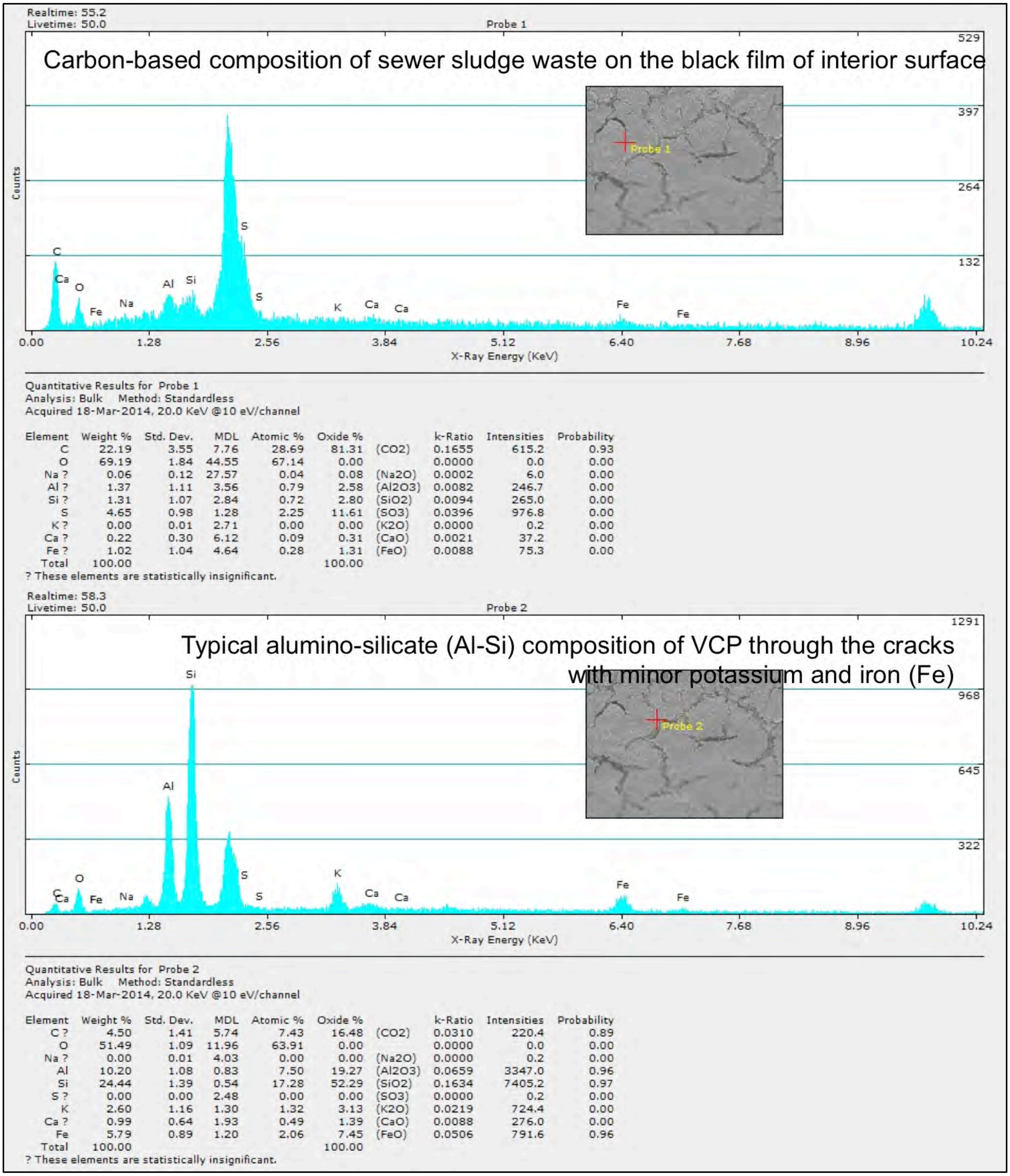


Figure 20: Sound interior pipe wall surface of 15-in. sound pipe.

This sample, therefore, shows the other end-member scenario of a typical VCP without intentionally incorporating any calcium minerals, where, few minor calcite grains in the original mud or clay clots of VCP cause gypsum formation in sewer acids (with local micro-blistering and pop out at the loci of such formation) but are nowhere near the scale in occurrence as in the case of intentional addition of calcium-minerals in the 33-in. pipe.

Elemental analysis from directly over dark gray dried sewer sludge film show a typical carbon-based (organic) composition of the sewer waste (Figure 21, unmarked peaks are for gold conductive coating), whereas, point-mode analyses from over a crack in the dried map-cracked sludge film shows typical alumino-silicate composition of the underlying vitrified clay matrix with minor amounts of potassium and iron, which are compositionally similar to the elemental composition of the clay matrix in the 33-in. pipe samples.

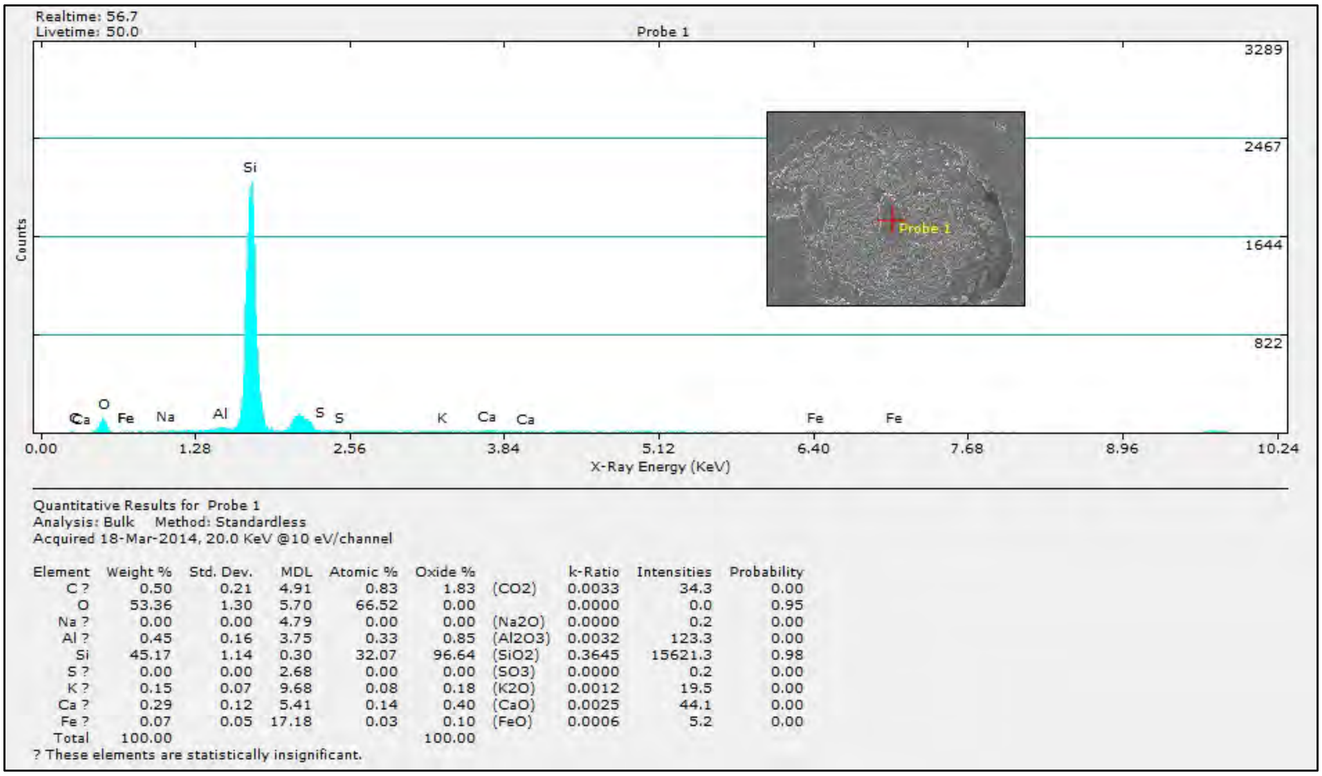


```
Quantitative Results for  Probe 1
Analysis: Bulk    Method: Standardless
Acquired 18-Mar-2014, 20.0 KeV @10 eV/channel

Element  Weight %  Std. Dev.   MDL  Atomic %  Oxide %           k-Ratio  Intensities  Probability
      C     22.19       3.55   7.76    28.69    81.31  (CO2)     0.1655        615.2         0.93
      O     69.19       1.84  44.55    67.14     0.00            0.0000          0.0         0.00
   Na ?      0.06       0.12  27.57     0.04     0.08  (Na2O)    0.0002          6.0         0.00
   Al ?      1.37       1.11   3.56     0.79     2.58  (Al2O3)   0.0082        246.7         0.00
   Si ?      1.31       1.07   2.84     0.72     2.80  (SiO2)    0.0094        265.0         0.00
      S      4.65       0.98   1.28     2.25    11.61  (SO3)     0.0396        976.8         0.00
    K ?      0.00       0.01   2.71     0.00     0.00  (K2O)     0.0000          0.2         0.00
   Ca ?      0.22       0.30   6.12     0.09     0.31  (CaO)     0.0021         37.2         0.00
   Fe ?      1.02       1.04   4.64     0.28     1.31  (FeO)     0.0088         75.3         0.00
  Total    100.00                               100.00
? These elements are statistically insignificant.
```

```
Quantitative Results for  Probe 2
Analysis: Bulk    Method: Standardless
Acquired 18-Mar-2014, 20.0 KeV @10 eV/channel

Element  Weight %  Std. Dev.   MDL  Atomic %  Oxide %           k-Ratio  Intensities  Probability
    C ?      4.50       1.41   5.74     7.43    16.48  (CO2)     0.0310        220.4         0.89
      O     51.49       1.09  11.96    63.91     0.00            0.0000          0.0         0.00
   Na ?      0.00       0.01   4.03     0.00     0.00  (Na2O)    0.0000          0.2         0.00
     Al     10.20       1.08   0.83     7.50    19.27  (Al2O3)   0.0659       3347.0         0.96
     Si     24.44       1.39   0.54    17.28    52.29  (SiO2)    0.1634       7405.2         0.97
    S ?      0.00       0.00   2.48     0.00     0.00  (SO3)     0.0000          0.2         0.00
      K      2.60       1.16   1.30     1.32     3.13  (K2O)     0.0219        724.4         0.00
   Ca ?      0.99       0.64   1.93     0.49     1.39  (CaO)     0.0088        276.0         0.00
     Fe      5.79       0.89   1.20     2.06     7.45  (FeO)     0.0506        791.6         0.96
  Total    100.00                               100.00
? These elements are statistically insignificant.
```

Figure 21: X-ray elemental analysis carbon-based sewer sludge waste on the black film of interior surface (top) and typical aluminosilicate matrix (bottom) of sound 15-in. VCP. Insets show backscatter elector images of wall from where analyses were done at the marked points.

Another analysis from over an argillaceous clay clot (ACC) mass show islands of small angular quartz crystals (Figure 22) surrounded by secondary gypsum masses (Figure 23) from reactions of small calcite grains in the clots (that are indeed unavoidable in those clots) with the sewer sulfuric acid. These gypsum masses in ACCs are small enough to prevent any large-scale pipe surface failure, instead of a few local blistering and popouts of ACCs.



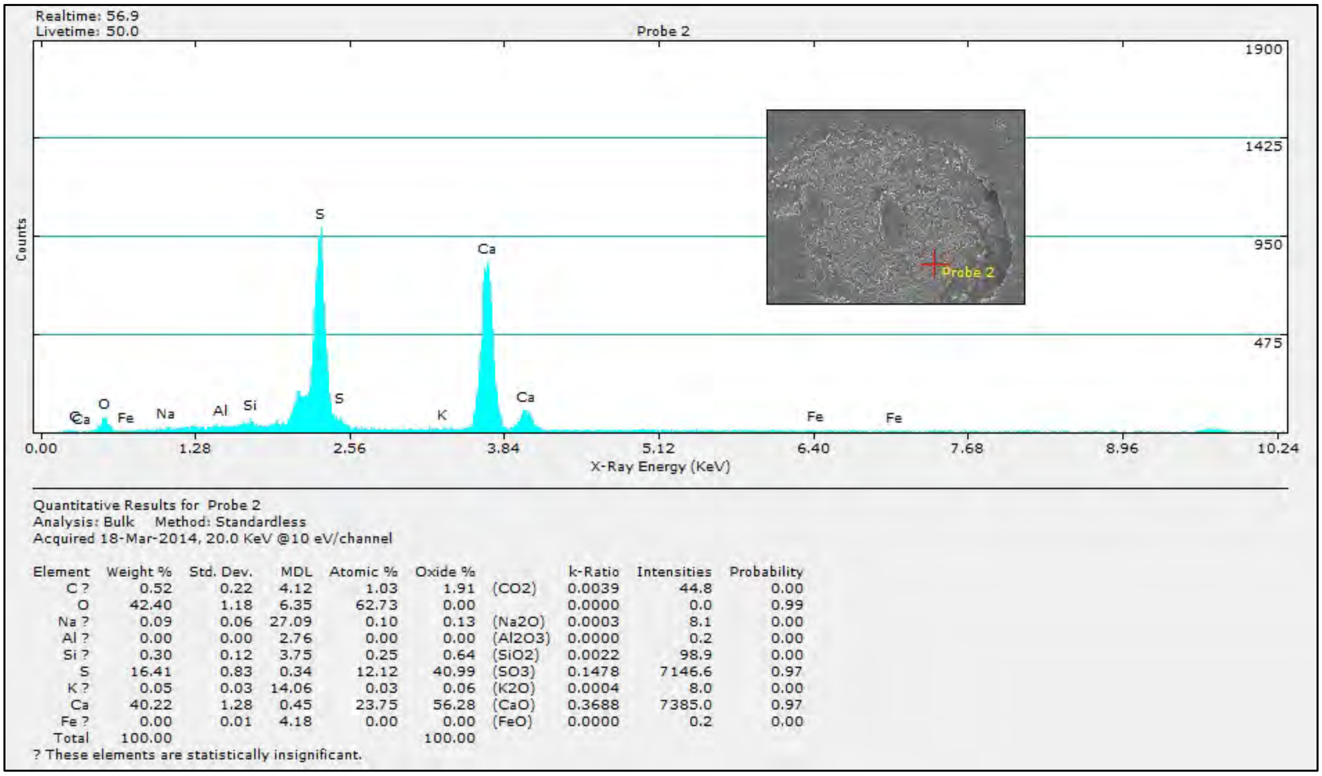
```
Quantitative Results for  Probe 1
Analysis: Bulk    Method: Standardless
Acquired 18-Mar-2014, 20.0 KeV @10 eV/channel

Element  Weight %  Std. Dev.   MDL  Atomic %  Oxide %           k-Ratio  Intensities  Probability
    C ?      0.50       0.21   4.91      0.83     1.83  (CO2)    0.0033        34.3         0.00
      O     53.36       1.30   5.70     66.52     0.00           0.0000         0.0         0.95
   Na ?      0.00       0.00   4.79      0.00     0.00  (Na2O)   0.0000         0.2         0.00
   Al ?      0.45       0.16   3.75      0.33     0.85  (Al2O3)  0.0032       123.3         0.00
     Si     45.17       1.14   0.30     32.07    96.64  (SiO2)   0.3645     15621.3         0.98
    S ?      0.00       0.00   2.68      0.00     0.00  (SO3)    0.0000         0.2         0.00
    K ?      0.15       0.07   9.68      0.08     0.18  (K2O)    0.0012        19.5         0.00
   Ca ?      0.29       0.12   5.41      0.14     0.40  (CaO)    0.0025        44.1         0.00
   Fe ?      0.07       0.05  17.18      0.03     0.10  (FeO)    0.0006         5.2         0.00
  Total    100.00                               100.00
? These elements are statistically insignificant.
```

Figure 22: X-ray elemental analysis from over an argillaceous clay clot (ACC) mass in sound 15-in. VCP from an islands of small angular quartz crystal as shown in the inset backscatter electron image.

Figure 24 shows the reddish brown vitrified clay matrix, which is essentially composed of silicon, aluminum, and minor amounts of potassium, and iron. Distributed throughout the vitrified clay matrix are very fine-grained (nominal 0.2 mm size) angular tempered quartz grains, such as one shown in Figure 25.

Sample from the sound 15-in. pipe demonstrated the importance of keeping any calcium-bearing phases in the VCP to an absolute minimum - to reduce the potential of any chemical deterioration of sewer pipe by deleterious chemical reactions between a calcium mineral and sewer gas (which is so common in the portland cement concrete sewer lines due to the abundance of calcium minerals in the portland cement hydration phases and in calcareous aggregates in concrete).

Furthermore, this sound pipe also explained the importance of not adding an intentional calcium additive to the VCP, irrespective of its any benefits, such as the observed wollastonite additive in the 33-in. line - since such calcium additive can cause deleterious chemical reactions with the sewer sulfuric acid to cause cracking and spalling of the pipe wall to the point of collapse.



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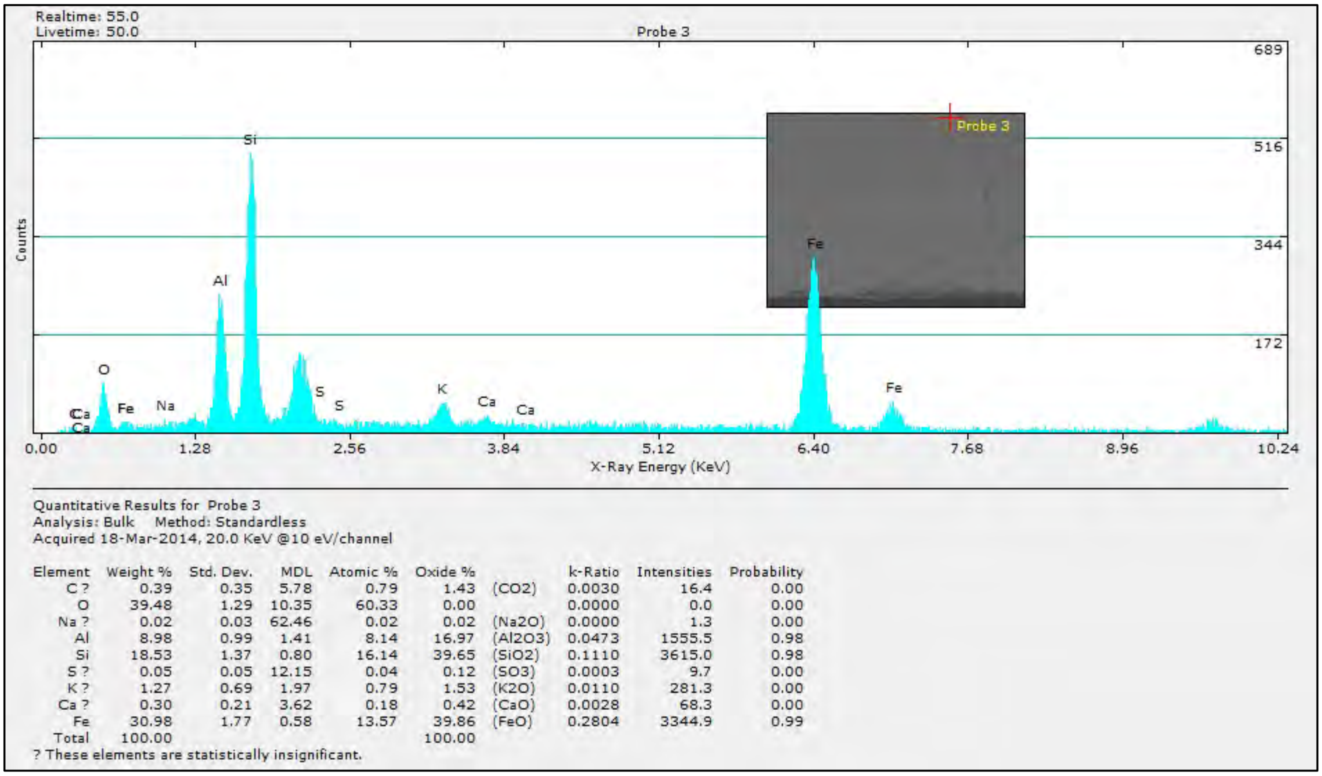
Quantitative Results for  Probe 2
Analysis: Bulk    Method: Standardless
Acquired 18-Mar-2014, 20.0 KeV @10 eV/channel

Element  Weight %  Std. Dev.   MDL  Atomic %  Oxide %          k-Ratio  Intensities  Probability
   C ?      0.52      0.22    4.12     1.03     1.91  (CO2)    0.0039       44.8        0.00
     O     42.40      1.18    6.35    62.73     0.00           0.0000        0.0        0.99
  Na ?      0.09      0.06   27.09     0.10     0.13  (Na2O)   0.0003        8.1        0.00
  Al ?      0.00      0.00    2.76     0.00     0.00  (Al2O3)  0.0000        0.2        0.00
  Si ?      0.30      0.12    3.75     0.25     0.64  (SiO2)   0.0022       98.9        0.00
     S     16.41      0.83    0.34    12.12    40.99  (SO3)    0.1478     7146.6        0.97
   K ?      0.05      0.03   14.06     0.03     0.06  (K2O)    0.0004        8.0        0.00
    Ca     40.22      1.28    0.45    23.75    56.28  (CaO)    0.3688     7385.0        0.97
  Fe ?      0.00      0.01    4.18     0.00     0.00  (FeO)    0.0000        0.2        0.00
 Total    100.00                              100.00
? These elements are statistically insignificant.
```

Figure 23: X-ray elemental analysis from over an argillaceous clay clot (ACC) mass in sound 15-in. VCP from secondary gypsum mass formed from reactions of small calcite grains in the clot, as shown in the inset backscatter electron image.



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Quantitative Results for  Probe 3
Analysis: Bulk    Method: Standardless
Acquired 18-Mar-2014, 20.0 KeV @10 eV/channel

Element  Weight %  Std. Dev.   MDL  Atomic %  Oxide %          k-Ratio  Intensities  Probability
   C ?      0.39      0.35    5.78     0.79     1.43  (CO2)    0.0030       16.4        0.00
     O     39.48      1.29   10.35    60.33     0.00           0.0000        0.0        0.00
  Na ?      0.02      0.03   62.46     0.02     0.02  (Na2O)   0.0000        1.3        0.00
    Al      8.98      0.99    1.41     8.14    16.97  (Al2O3)  0.0473     1555.5        0.98
    Si     18.53      1.37    0.80    16.14    39.65  (SiO2)   0.1110     3615.0        0.98
   S ?      0.05      0.05   12.15     0.04     0.12  (SO3)    0.0003        9.7        0.00
   K ?      1.27      0.69    1.97     0.79     1.53  (K2O)    0.0110      281.3        0.00
  Ca ?      0.30      0.21    3.62     0.18     0.42  (CaO)    0.0028       68.3        0.00
    Fe     30.98      1.77    0.58    13.57    39.86  (FeO)    0.2804     3344.9        0.99
 Total    100.00                              100.00
? These elements are statistically insignificant.
```
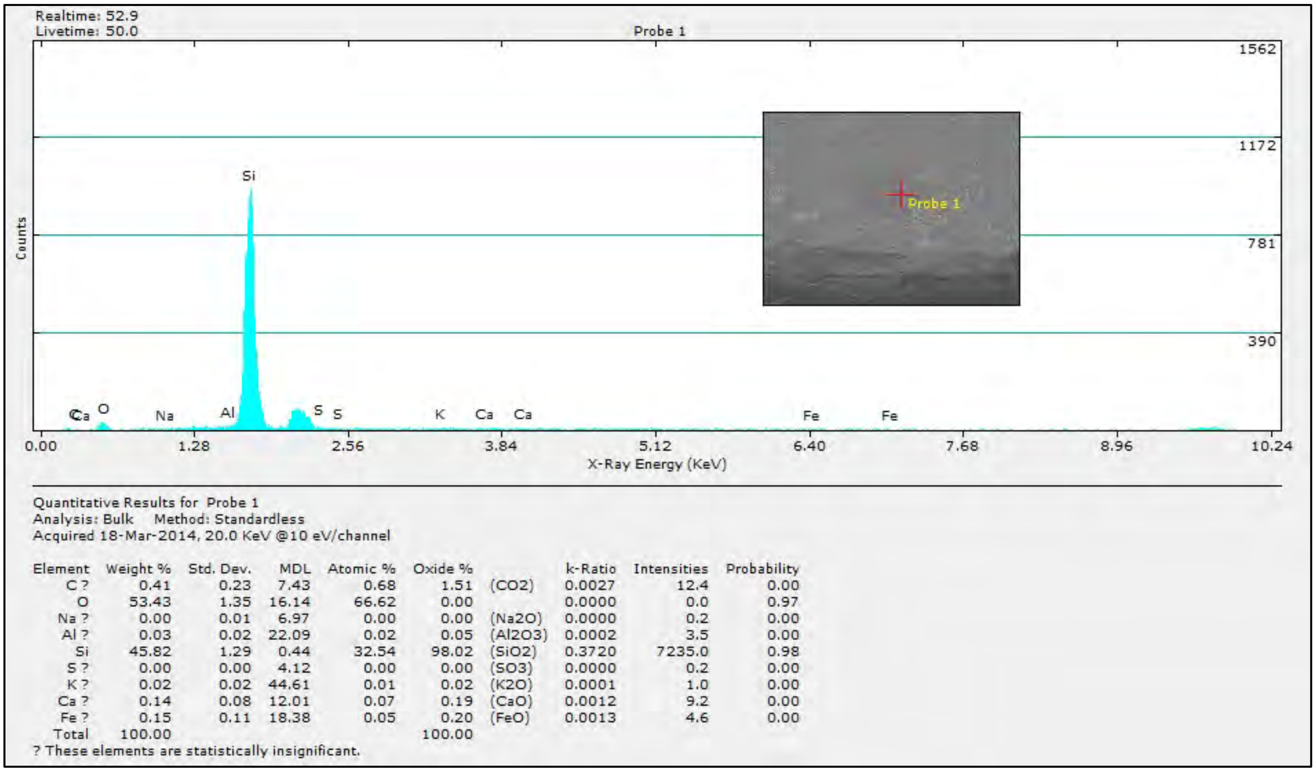

Figure 24: X-ray elemental analysis of reddish brown vitrified clay matrix essentially composed of silicon, aluminum, and minor amounts of potassium, and iron.



Quantitative Results for Probe 1
Analysis: Bulk Method: Standardless
Acquired 18-Mar-2014, 20.0 KeV @10 eV/channel

Element	Weight %	Std. Dev.	MDL	Atomic %	Oxide %		k-Ratio	Intensities	Probability
C ?	0.41	0.23	7.43	0.68	1.51	(CO2)	0.0027	12.4	0.00
O	53.43	1.35	16.14	66.62	0.00		0.0000	0.0	0.97
Na ?	0.00	0.01	6.97	0.00	0.00	(Na2O)	0.0000	0.2	0.00
Al ?	0.03	0.02	22.09	0.02	0.05	(Al2O3)	0.0002	3.5	0.00
Si	45.82	1.29	0.44	32.54	98.02	(SiO2)	0.3720	7235.0	0.98
S ?	0.00	0.00	4.12	0.00	0.00	(SO3)	0.0000	0.2	0.00
K ?	0.02	0.02	44.61	0.01	0.02	(K2O)	0.0001	1.0	0.00
Ca ?	0.14	0.08	12.01	0.07	0.19	(CaO)	0.0012	9.2	0.00
Fe ?	0.15	0.11	18.38	0.05	0.20	(FeO)	0.0013	4.6	0.00
Total	100.00				100.00				

? These elements are statistically insignificant.

Figure 25: Fine-grained (nominal 0.2 mm size) angular tempered quartz grains scattered over the vitrified clay matrix in sound pipe.

CONCLUSIONS

Comparative petrographic examinations of saw-cut samples from both the distressed 33-in. and the sound 15-in. VCPs – both experiencing similar sewer environments have demonstrated the importance of careful control of the original VCP pipe compositions in resisting any potentially deleterious chemical reactions of VCP from sewer gases and acids. Both pipes, reportedly, manufactured by the same manufacturer, clearly demonstrated better performance of an older pipe at the sewer environment exposed to longer periods of sewer gases but still performing in sound condition because of lack of any major calcium minerals in the pipe to participate in any deleterious reaction with the sewer gases, as opposed to intentional addition of a calcium mineral (wollastonite) and its ready dissolution and participation in chemical reaction with sewer sulfuric acid to cause expansive formation of gypsum, silica gel, and subsequent cracking, spalling, and loss of cross sectional thickness of the pipe wall to the point of pipe collapse.

Besides the VCP composition, the degree of deterioration of a pipe is also dependent on the availability and amount of deleterious sewer gases and acids, moisture content, and flow of sledges to continuously replenish fresh VCP wall to participate in deleterious reactions. The present study, however, demonstrated that the basic composition of the VCP plays a pivotal role in controlling the occurrence and extent of VCP distress in a sewer environment.

Table 1: Petrographic Descriptions of Three Samples of the 33-in. distressed VCP

	Materials & Components of 33-in. VCP Samples	**Sample ID# 001 Lab #001**	**Sample ID# 001 Lab #002**	**Sample ID# 002 Lab# 1**
1	**Nonplastic Components**			
	a. *Mineral Fragments (sand)*, natural or tempered additive to improve workability/plasticity of clay, and good drying an firing qualities, thermal shock resistance, improve toughness); mono and/or polycrystalline quartz is most common, 0.05 to 2 mm in nominal size	i) Natural and tempered quartz grains, angular, quant, mono and polycrystalline quartz, nominal 0.2 mm in size ii) Natural feldspar grains, prismatic, subhedral, angular, nominal 0.4 mm in size iii) Tempered long slender prismatic clear crystals of wollastonite (calcium metasilicate, $CaSiO_3$) additives distributed all over the body, smaller than clay clots, subhedral to euhedral, 0.4 mm long size iv) Natural mafic minerals, e.g., pyroxenes, subangular, lath-shaped, nominal 0.5 mm in size	i) Natural and tempered quartz grains, angular, quant, mono and polycrystalline quartz, nominal 0.2 mm in size ii) Natural feldspar grains, prismatic, subhedral, angular, nominal 0.4 mm in size iii) Tempered long slender prismatic clear crystals of wollastonite (calcium metasilicate) additives distributed all over the body, smaller than clay clots, subhedral to euhedral, 0.4 mm long size iv) Natural mafic minerals, e.g., pyroxenes, subangular, lath-shaped, nominal 0.5 mm in size	i) Natural and tempered quartz grains, angular, quant, mono and polycrystalline quartz, nominal 0.2 mm in size ii) Natural feldspar grains, prismatic, subhedral, angular, nominal 0.2 mm in size iii) Tempered long slender prismatic clear crystals of wollastonite (calcium metasilicate) additives distributed all over the body, smaller than clay clots, subhedral to euhedral, 0.4 mm long size iv) Natural mafic minerals, e.g., pyroxenes, subangular, lath-shaped, nominal 0.4 mm in size
	b. *Rock/Lithic Fragments*, natural or tempered additive	i) Natural siltstone grains, subrounded, nominal 1 mm in size	i) Natural siltstone grains, subrounded, nominal 0.5 mm in size	i) Natural siltstone grains, subrounded, nominal 0.5 mm in size
	c. *Argillaceous Clay/Rock Fragments*, ACF/ARF (Argillaceous Clay Clots ACC, Argillaceous Rock Fragments, ARF, and/or Hematite-Stained Clay Clots, HCC) – Original or tempered additive	i) ACC, rounded, nominal 3 mm in size, few ARFs ii) HCC, rounded, 1 mm in nominal size	i) ACC, rounded, nominal 3 mm in size, few ARFs ii) HCC, rounded, 1 mm in nominal size	i) ACC, rounded, nominal 3 mm in size, few ARFs ii) HCC, rounded, 1 mm in nominal size
	d. *Grog* (tempered additive of previously fired ceramic fragments for close properties and compositions of clay matrix)	Grog particles dark reddish brown, nominal 1 mm, rounded	Grog particles dark reddish brown, nominal 1 mm, rounded	Grog particles dark reddish brown, nominal 1 mm, rounded
	e. *Calcium Carbonate* (e.g., shell fragments, carbonate rocks) natural, or, tempered additive for improving drying and firing properties of clay by increasing porosity, serving as a flux to lower fusing temperature of clay)	None	None	None
	f. *Organics* (e.g., plant fiber, seeds, husks, textile fragments, animal products, feathers, straw, stems of crop plants, petrified wood, etc.) – tempered additive to improve plasticity, workability, and fabrication of clay control shrinkage during drying, etc.)	None	None	None

	Materials & Components of 33-in. VCP Samples	Sample ID# 001 Lab #001	Sample ID# 001 Lab #002	Sample ID# 002 Lab# 1
	g. *Other Additives* (Mica, salt, slag, ash, etc. as tempered additives)	None	None	None
2	**Plastic (Clay) Components & Firing Conditions**			
	a. *Vitrified clay matrix* – Amorphous and/or semi-crystalline	Amorphous aluminosilicate vitrified clay matrix	Amorphous aluminosilicate vitrified clay matrix	Amorphous aluminosilicate vitrified clay matrix
	b. *Vitrified clay matrix* – Hematite-stained or Not	Hematite-stained vitrified clay – uniform color of matrix	Hematite-stained vitrified clay, outer (1/2 to 3/4 in.) edges of clay pipe are lighter toned than the inner portion	Hematite-stained vitrified clay, outer (1/2 to 3/4 in.) edges of clay pipe are lighter toned than the inner portion
	c. *Vitrified clay matrix* – Other Properties	Uniform properties, porosity, across the thickness of the pipe sample	Uniform properties, porosity, across the thickness of the pipe sample, except for the central zone of darker matrix as patches of darker matrix as described before	Uniform properties, porosity, across the thickness of the pipe sample, except for the central zone of darker matrix as patches of darker matrix as described before
3	a. *Firing Conditions* – Oxidizing vs. Reducing	More or less uniformly oxidizing condition during and after firing throughout the entire thickness of the pipe	Outer edges experienced more oxidizing condition during and after firing than the inner portion of pipe	Outer edges experienced more oxidizing condition during and after firing than the inner portion of pipe
	b. *Firing Conditions* – High vs. Low Temperature	Uniform firing temperatures throughout the entire thickness of the pipe	Outer edges experienced higher firing temperature than the inner portion of pipe	Outer edges experienced higher firing temperature than the inner portion of pipe
	c. *Firing Conditions* – High vs. Low Carbon Content			
4	**Void Contents, %**	2.9 (from image analysis)	1.1 (from image analysis)	-
5	**Secondary Alterations**	Along the spalled interior surface showing alteration of tempered wollastonite additive to gypsum and silica gel	None	Along the spalled interior surface showing alteration of tempered wollastonite additive to gypsum and silica gel
6	**Efflorescence Deposits**	Spotted and pitted white secondary deposits on the spalled interior surface - gypsum and silica gel	No visible efflorescence salt deposits on the inner or outer surfaces or within the pipe sample	Spotted and pitted white secondary deposits on the spalled interior surface - gypsum and silica gel
7	**Visible Distress, Cracking**	Visible cracks within the bottom 1 to 1 1/4 in. distance of the inner spalled surface of the pipe	No visible cracks throughout the thickness of the pipe	Cracks near the spalled interior to a distance of 2 to 4 mm
8	**Other Properties**	Distressed sample with scaled and spalled interior surface and formed sound exterior surface Nominal thickness – 2 1/2 in. Lateral Dimension – 12 1/2 × 9 1/2 in.	Sound and formed interior and exterior surfaces Nominal thickness – 3 1/4 in. Lateral Dimension – 10 1/2 × 10 in.	Distressed sample with scaled and spalled interior surface and formed sound exterior surface Nominal thickness – 2 1/2 in. Lateral Dimension – 13 1/2 × 12 in.

Table 2: Petrographic Descriptions of 15-in. sound VCP Components

	Materials & Components of VCP	**15-in. VCP Sample**
1 Non-plastic Components		
	a. *Mineral Fragments (sand)*, natural or tempered additive to improve workability/plasticity of clay, and good drying an firing qualities, thermal shock resistance, improve toughness); mono and/or polycrystalline quartz is most common, 0.05 to 2 mm in nominal size	i) Natural and tempered quartz grains, angular, quant, mono and polycrystalline quartz, nominal 0.2 mm in size ii) Vesicular slag particles, 1 mm in nominal size
	b. *Rock/Lithic Fragments*, natural or tempered additive	i) Natural siltstone grains, subrounded, nominal 1 mm in size
	c. *Argillaceous Clay/Rock Fragments*, ACF/ARF (Argillaceous Clay Clots ACC, Argillaceous Rock Fragments, ARF, and/or Hematite-Stained Clay Clots, HCC) – Original or tempered additive	i) ACC, rounded, nominal 3 mm in size, few ARFs ii) HCC, rounded, 1 mm in nominal size
	d. *Grog* (tempered additive of previously fired ceramic fragments for close properties and compositions of clay matrix)	Grog particles dark reddish brown, nominal 1 mm, rounded
	e. *Calcium Carbonate* (e.g., shell fragments, carbonate rocks) natural, or, tempered additive for improving drying and firing properties of clay by increasing porosity, serving as a flux to lower fusing temperature of clay)	None, except perhaps a very few tiny calcite grains in the ACCs
	f. *Organics* (e.g., plant fiber, seeds, husks, textile fragments, animal products, feathers, straw, stems of crop plants, petrified wood, etc.) – tempered additive to improve plasticity, workability, and fabrication of clay control shrinkage during drying, etc.)	None
	g. *Other Additives* (Mica, salt, slag, ash, etc. as tempered additives)	None
2 Plastic Components		
	a. *Vitrified clay matrix* – Amorphous and/or semi-crystalline	Amorphous aluminosilicate vitrified clay matrix
	b. *Vitrified clay matrix* – Hematite-stained or Not	Hematite-stained vitrified clay – uniform color of matrix
	c. *Vitrified clay matrix* – Other Properties	Uniform properties, porosity, across the thickness of the pipe sample
3	a. *Firing Conditions* – Oxidizing vs. Reducing	Relatively darker tone of matrix along the center compared to lighter reddish brown tone along the outer edges, indicating relatively higher firing temperature of pipe and/or more oxidize conditions during firing along the outer (exterior and interior) edges than in its inner central zone
	b. *Firing Conditions* – High vs. Low Temperature	Uniform firing temperatures throughout the entire thickness of the pipe
	c. *Firing Conditions* – High vs. Low Carbon Content	
4	**Void Contents, %**	2.6 (from image analysis)
5	**Secondary Alterations**	None
6	**Efflorescence Deposits**	None
7	**Visible Distress, Cracking**	None
8	**Other Properties**	Sound sample having sound interior surface and formed sound exterior surface Nominal thickness – $1\frac{1}{2}$ in. Lateral Dimension – $7\frac{1}{4}$ × 7 in.

REFERENCES

1. Jana, D., and Lewis, R. A., Acid Attack in a Concrete Sewer Pipe – A Petrographic & Chemical Investigation, 27th Conference of International Cement Microscopy Association, 2005.
2. Vitrified Clay Pipe, from Wikipedia, The Free Encyclopedia.
3. ASTM C 1208/C1208M-11 Standard Specification for Vitrified Clay Pipe and Joints for Use in Microtunneling, Sliplining, Pipe Bursting, and Tunnels, American Society for Standards and Materials, Subcommittee C04.20, Volume 4.05.
4. ASTM C 12-13, Standard Practice for Installing Vitrified Clay Pipe Lines, American Society for Standards and Materials, Subcommittee C04.20, Volume 4.05.
5. ASTM C 301-13 Standard Test Methods for Vitrified Clay Pipe, American Society for Standards and Materials, Subcommittee C04.20, Volume 4.05.
6. Pipe Penetrating Radar, in SewerVUE In-Pipe GPR, www.sewervue.com
7. Fernandez-Caliani, J.C., Barba-Brioso, C., and Perez-Lopez, R., Long-term interaction of wollastonite with acid mine water and effects on arsenic and metal removal, Applied Geochemistry, Vol. 23, pp. 1288-1298, 2008.