Corrosion, Prevention and Cure to Concrete Sewage Pipes

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Abstract: Urban sewage causes blow-off lines that are made from concrete to erode seriously over time, as a result, various countries around the world poured huge material and financial resources into researching this problem. The erosion occurs chiefly due to SO_4^{-2} that is induced by complicated biochemical reactions, which are decomposition & oxidation-reduction reaction by microbes and organisms in sewage.

Chief ways of solving this problem is to coating concrete pipes with waterproof and anticorrosive materials. One of the best is CN2000 high efficiency waterproof material. CN2000B（CCCW） is the first choice for these type of materials.

Key words: *urban sewage; concrete; microbe; hydrogen sulfide; sulfate radical; waterproof; anticorrosive*

1. Origin and Importance of the Microbe Problem

There are many and various kinds of microbes in industrial and urban sewage. The erosion due to the metabolism of microbes in concrete is called microbe corrosion of concrete. The microbe erosion may cause the surface mortar of the concrete structure of facilities treating sewage to fall out and the aggregate to be exposed. When there is serious exposure, the concrete will crack and the steel bar will be corroded. This will decrease the facilities service life greatly. This not only influences the global function of a city, directly but consumes great material and financial resources on its rebuilding and repairing of this important infrastructure.

Investigation shows that the destruction due to microbe erosion is a significant part of building material destruction in all parts of the world. As one of the earliest used products, the concrete pipes do not protect from damage suffered from microbe erosion. In the early years of the 19th century, samples of destruction of sewage pipeline systems suffering from corrosion were found in Los Angeles, Cairo, Cape Town, and Melbourne, and in many other cities.

However these destructive forces were not viewed as seriously as the erosion of acid or salt to concrete. This phenomenon was not paid attention to by engineering circles until the middle of the last century, after a series of microbe erosion cases to serving concrete pipes had taken place in succession.

According to the report, the cost of repairing the sewage concrete pipe system in Hamburg, Germany, which suffered from thio-bacillus erosion, was more than 50 million Marks in the 1970's.

In 1959, Pomeroy investigated microbe erosion in 3100 kilometers of sewage line of the drainage system which had served 35 years in the city of Los Angeles in California. It was found that 0.25% of the pipe line (7.5 kilometers) suffered from microbe erosion.

In 1989, investigation of the drainage system of Houston, Texas showed that the cost to restore damaged sewage pipe line, was estimated at about 47.70 million U.S. dollars. The destruction of 70% of the damaged pipes was found to be a result of hydrogen sulfide erosion.

Other countries such as Japan, Germany and Australia are all facing similar problems. Recently, in China there were similar cases discovered. Recent investigations of sewage treatment facilities which began operating in the mid 1980's showed that due to concrete suffering from microbe erosion, the sewage treatment plant had extensive corrosion damage and is not expected to reach its designed service life. Other sewage treatment facilities which began operating in the 1990's have been observed as having obvious corrosion phenomenon at this time.

In view of its severe harmfulness, the microbe erosion to concrete has been taken into account by western countries long ago. The mechanism and control measures have been studied extensively. In 1945, in Melbourne, Parker indicated that the corrosion of sewage concrete pipes was a result of microbes.

A multi-disciplinary organization has been established in Germany which has made a synthesis investigation into microbe erosion. They have investigated and discussed various projects in California, Australia, Africa, Middle East, Near East, South America and Singapore, and believe that the problem of microbe erosion to material comes down to such a multi-disciplinary, intersection of sciences challenge, and requires the expertise of biologists, chemists, material scholars and even structural experts.

2. Research of the Corrosion Mechanism

2.1 Erosion Factors

In the Chinese National Standard GB8979 "Integrated Wastewater Discharge Standard" the pollutants are divided into two types: the first, are those that cause long term adverse effect to human health, such as mercury, arsenic cadmium, and lead etc., which discharges are required to be strictly controlled.

The second type are those that cause less effect to human health than first, in which the suspended substance (SS), biochemical oxygen demand (BOD_5) chemical oxygen demand (COD), pH value, sulfide and phosphate etc. All have potential erosive actions to concrete. The standard stipulates different allowable discharge amounts to each different pollutant. For the latter the stipulated standard is as follows,

Table 1 the standard value for a part of second kind of pollutant (mg/L)

Pollutant	Third class standard
pH	6~9□
Suspended matter / (mg/L)	400
BOD_5/(mg/L)	300
COD/(mg/L)	500
Sulfide / (mg/L)	2.0

□ is dimensionless unit

2.2 Erosion Mechanism

2.2.1 Chemical Erosion

2.2.1.1. Dissociated CO_2

High alkalinity of concrete is very important for the stability of cement hydration product. All the acid matter in the environment such as CO_2, acid rain and acid water etc. will react with the alkaline substance in the concrete, and make concrete carbonized (neutralized) to cause cement hydration product decomposed and to make the strength of the concrete decreased, and even losing strength altogether. The carbonizing reaction is as follows,

$$CO_2 + H_2O + Ca(OH)_2 = CaCO_3\downarrow + 2H_2O$$
$$CaCO_3 + CO_2 + H_2O = Ca(HCO_3)_2$$

When the hardness of sewage is less and the CO_2 content is high, erosion to concrete is aggravated.

The lowest alkalinities for cement hydration products to keep stable are as stated in following table,

Table2: The least pH value for cement hydration products to keep stable

Cement hydration product	Critical pH
$2CaO \cdot SiO_2 \cdot 7H_2O$	11.2
$6CaO \cdot 6SiO_2 \cdot H_2O$	10.67
$5CaO \cdot 6SiO_2 \cdot 5H_2O$	10.0
$2CaO \cdot 3SiO_2 \cdot 2.5H_2O$	9.78
$4CaO \cdot Al_2O_3 \cdot 19H_2O$	8.15
$3CaO \cdot Al_2O_3 \cdot CaSO4 \cdot 12H_2O$	7.95

At the same time centralization of concrete makes the steel bar lose protection. When the pH<11.5, it will induce corrosion of the steel bar.

2.2.1.2. Erosion of Sulfate

In cities there are different levels of sulfate for different sewage. The sulfate content in sanitary sewage usually is 20~100 mg/L; however discharge of industrial waste water increases the sulfate level greatly. Even through treating the content of $(SO_4)^{-2}$ is still about 2000 mg/L. According to the Chinese national relative standard "Engineering Construction Quality Acceptance Standard of Railway Concrete and Masonry" (TB10420-2003) and "The Erosion Classification Standard for Harmful Ions in Water (for Reinforced Concrete)" about the standard of erosion type and erosion degrees of environment water to concrete such a content of $(SO_4)^{-2}$, 2000 mg/L, has reached to middle erosion.

According to different composition of sulfate, erosion to concrete has a "dilation type", "crystalline type", and "decomposition type" so on many kinds of erosion. They destruct concrete structures severely. At the same time $(SO_4)^{-2}$ has erosion action to steel bar also.

2.2.1.3. Erosion of Hydrogen Sulfide

Hydrogen sulfide gas can be dissolved in water and becomes an acid. Its solubility in water is minimal, and shows weak acidity; a large part of un-disassociated hydrogen sulfide will escape from the water. Ionization of hydrogen sulfide in water is as follows,

$$H_2S \rightleftharpoons H^+ + HS^- \qquad K_1 = 5.7\times10^{-8}$$

$$HS^- \rightleftharpoons H^+ + S^{2-} \qquad K_2 = 1.2\times10^{-15}$$

This ionization balance depends greatly on pH value of the solution. When acidity or $[H^+]$ is high, the direction of ionization will go to the left. It is reported that when pH=7, the contents of HS^- and H_2S are almost equal to each other and at about 50%, when pH=6, the content of H_2S in water increases to about 90%, in this situation H_2S will mostly escape from the water.

Hydrogen sulfide acid or H_2S gas with the existence of water will cause concrete neutralization and bring about electrochemical erosion to concrete or makes it in hydrogen embrittlement.

2.2.2 Microbe Erosion

When people hadn't understood the microbe erosion to concrete, they often considered that the erosion to sewage pipes was simply due to the chemical erosion of acids and salts in the sewage as stated above. However after analysis it is shown that the inorganic acid and salt content in sewage isn't sufficient to cause such serious destruction to concrete waste disposal pipe. In fact, microbe erosion progresses in a complicated biochemical reaction mechanism. The existence of microbes and a particular environment is an indispensable condition for concrete sewage pipe to suffer from this serious corrosion.

2.2.2.1 Environmental Condition

In table 1 the listed suspended substance (SS), biochemical oxygen demand (BOD) and chemical oxygen demand (COD) as well as feasible pH establish condition for microbes to grow and breed.

Different pH values are suitable to different microbes growing. The optimal pH for aerobe is 6.5~7.5; the optimal pH for anaerobe is 6.7~7.4. Along with the environment temperature going, up the optimal pH will also rise.

Suspended substances are the inorganic and organic particles, and also include settled solid particles. They often become a concealed carrier of microbes.

When organic particles subside to the bottom, they will consume dissolved oxygen in the water, and make the creature density in the silt increase, which creates favorable conditions for microbe erosion.

Biochemical oxygen demand (BOD) and chemical oxygen demand (COD) are a synthesized index of organic pollution for sewage and industrial waste water. They all reflect consumed the oxygen amount that the organisms in sewage and industrial waste water require for oxygenolysis. The difference, is that the BOD is the oxygen demand for oxygenolysis under microbe actions in a certain period under a constant temperature of 20°C, which represents the consumed oxygen amount on the part of organisms in sewage that can be biodegraded, and COD is the one under chemical oxidizer action which represents consumed one that can be decomposed by a chemical oxidizer. In fact these two indexes reflect the amount of organisms in sewage, by the consumed oxygen amount indirectly. The biochemical oxygen demand and chemical oxygen demand play a decisive role on the process of microbe erosion to concrete pipes.

2.2.2.2 Erosion Mechanism

The mechanism of microbe erosion to concrete is very complicated, and has a number of types. They include the erosive destruction by inorganic acids (such as sulfate, sulfurous acid and carbonic acid etc.), and organic acids (such as formic acid, acetic acid and isovalerate etc.) secreted by microbes (aerobe) in production from metabolism; The erosive destruction of the salts produced through the reactions of the above noted acids with action in the cement stone; The complex compound produced by reaction of organic acid with the action; And the one of hydrogen sulfide and creature membrane generated by anaerobe. The researcher found out that there are 40 different kinds of bacteria participating in this erosion. Because microbes breed very fast, they cause the pH of sewage near concrete to decrease to 6 from the original 12~13.

To make the problem simpler and more concentrated, we will discuss it under the mechanism put forward by the Australian, Thistlethwayte, see the following sketch.

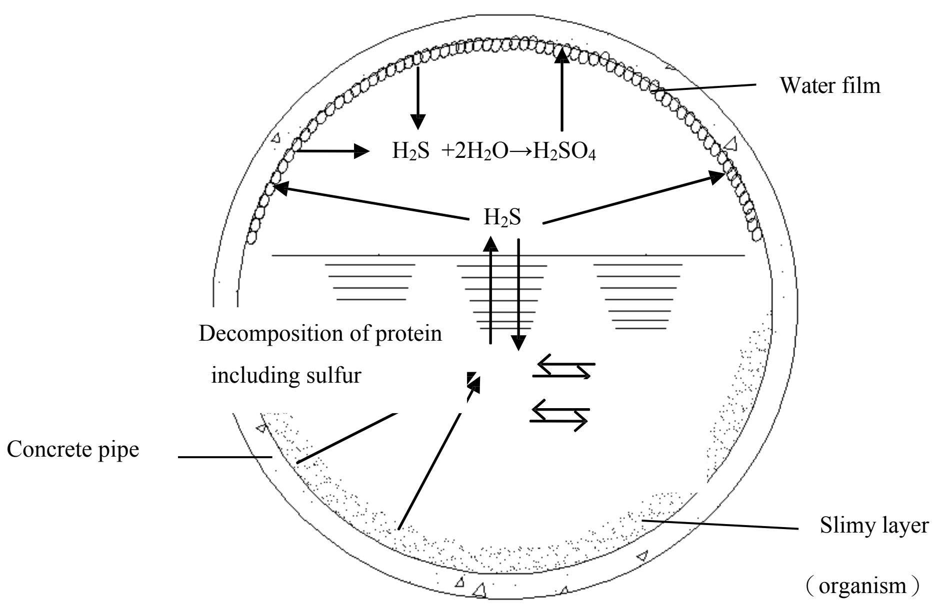


Fig 1 the mechanism of erosion of sewage to walls of concrete pipes

The erosion by microbes to concrete pipes is a dynamic process. In fact they are series of complicated biochemical reactions focused on oxidation-reduction under the action of microbes. The suspended substance in sewage and waste water deposit gradually along with the water flow on the bottom of the pipe and become a slimy layer; the organism becomes a nutrient source to microbes; Under oxygen-poor conditions, anaerobe beaks down the organisms and snatches its carbon to form a colorless and flavorless methane, but with organic sulfide the product will become hydrogen sulfide gas. For example, a protein containing cysteine, after decomposition and devulcanization by bacteria will release hydrogen sulfide. The reaction is as follows,

$$HOOCCH(NH_2)CH_2SH + H_2O \rightarrow CH_3COCOOH + H_2S + NH_3$$

The another way to generate hydrogen sulfide is that under oxygen-poor conditions the sulfate reducing bacteria snatch oxygen from sulfates, and consume the organisms and metabolize to generate hydrogen sulfide. The reaction is as follows,

$$SO_4^{2-} + 2(CH_2O) + 2H^+ \rightarrow H_2S + 2CO_2 + 2H_2O$$

Hydrogen sulfide generated in the above two ways, escapes from the sewage and enters into the pipes air space and contacts the pipe wall, and dissolves in the water film condensed on the wall; while on the wall, the hydrogen sulfide suffers a biochemical action of the aerobes: thio-bacteria oxidizes the hydrogen sulfide and produces sulfur, while thiobacillus oxidizes sulfur and produces sulphuric acid; the reaction is as follows,

$$H_2S + H_2O \rightarrow H_2SO_4$$

The above process is a one kind of a natural sulfur cycle under this particular environment. The generated erosion to concrete is called the biological sulfuric acid corrosion. All the sulfuric acid and various other inorganic, organic acid generated during these process will cause the concrete layer on the pipe wall to be neutralized or carbonized, decomposing its CSH gel and destructing the concrete.

The above theory has been confirmed by studies done by Roberson and Paintal.

Generally speaking, for the inner concrete wall of sewage pipe, below the sewage liquid level, concrete suffers mainly from erosion of the weak acids generated by the metabolism of microbes in the sewage; above the liquid level, in addition to weak acid, concrete also suffers from erosion of hydrogen sulfide and sulfuric acid generated through the microbe oxidation; the biological film at the interface between the air and liquid is the optimum environment for bacteria growth, where microbes breed prolifically and live in the porous concrete causing erosion to penetrate deeply; and due to the washing out of the sewage flow, the concrete suffers the superimposed effect of multiple erosion factors and the corrosion of concrete here is most severe.

Erosion from microbes on concrete has various forms which act not only independently, but cooperatively, and synthesize each other; furthermore various kinds of physical and chemical erosions to concrete are often strengthened due to the existence and metabolism of microbes.

For example, the accumulation and metabolism of microbes increases the content of the water in the void of the concrete. It aggravates the freeze-thaw destruction to concrete and therefore the microbe erosion plays a significant role in concrete pipe corrosion.

2.2.2.3 Influence factors

From the above noted biochemical process, it can be seen, that the source of the production and the escape of hydrogen sulfide and sulfuric acid from its oxidation has come down to the reduction of anaerobe to organism. The study shows that the factors that affect this process include temperature, humidity, ventilation, pH value, biochemical oxygen demand (BDO), light ray, COD/ SO_4^{2-} (C/S) as well as water-chemistry and liquid dynamics and so forth. Here we cannot stress the details more than is necessary. In brief, the environment in sewage pipes creates very suitable conditions for microbes to grow, breed, and cause biochemical actions.

2.3 Survey of Corrosion Status

2.3.1 Determining the Position

The erosion of hydrogen sulfide usually happens in the following positions: the position where the slope is minimal, where the flow rate is slow and retention time is lengthy; at inspection wells; at the point for current discharge; and at places where the sewage flow is in a turbulent state.

2.3.2 Procedure of Investigation

a) Collect and analyze the basic information: chart of sewage pipe network; note the positions which have been repaired previously; the point where hydrogen sulfide gas escapes and so forth.
b) Preliminary investigation: visual inspection as to the appearance of features (Note: Before going into pipes for inspection, safety and precautionary measures should be taken to protect workers from poisoning); the hydrogen sulfide gas content in the atmosphere; DO value in sewage, sulfide concentration and pH value; the pH

value in the space over the water level and near the pipe wall.

c) Investigation in detail: corrosion product; corrosion depth.
d) Evaluate corrosion levels and determine further detecting range and contents.

3. Counter Measures

The study of microbe erosion to concrete is an inter-disciplinary subject referring to material sciences, microbe science, biochemistry and civil engineering and other disciplines.

At the present time, the mechanism of the microbe erosion, especially the effect of biofilm to corrosion dynamics of concrete still needs to be studied further; and the radical purpose of study will be to establish effective counter-measures, and ensure sewage facilities reach their designed service life. Now, to seek an effectual counter-measure to protect microbe erosion to concrete is common concern for scholars of various countries. The mechanism of microbe erosion to concrete can be summarized as follows: under anaerobic conditions, sulfate reducing bacteria reduces sulfate or organic sulfur on the bottom of the pipe and produces hydrogen sulfide, then hydrogen sulfide enters into the space above the sewage within the concrete pipe; under aerobic conditions, sulfur reducing bacteria oxidizes sulfur, and turns it into a biological sulfuric acid, which then penetrates into the concrete and when combined with $Ca(OH)_2$ it reacts to produce gypsum, this makes the cement hydrate (CSH) decompose and produce insoluble and non-adhering colloid SiO_2, while gypsum reacts with the hydrate of C_2A and then produce ettringite. The production of ettringite accompanies volume expansion, which causes concrete to crack and speeds up the corrosion destruction of the concrete wall. So only under aerobic condition can H_2S be oxidized by oxidizing bacteria into biological sulfuric acid and a strong corrosion to concrete is caused.

Theoretically, increasing the resistance abilities of sulfuric acid erosion to gelatinous material, controlling corrosion mass transport process and inhibiting or decreasing generation of biological sulfuric acid can all help to relieve microbe erosion to concrete.

Therefore, the current counter-measures of protecting concrete from microbe erosion include three main processes: modification of concrete; surface layer protection and controlling the nutrient source of microbes in sewage; and a bacteria sterilization technique. The first two measures play a principal and essential role, which are the focus that we concern ourselves with and will discuss.

The modification of concrete includes - increasing anti-acid, impervious and anti-cracking ability.

The method of increasing anti-acid ability is to change the composition and structure of the concrete. The main purpose is to increase the resistance of centralization of concrete and to slow down the corrosion process; the major purpose is to enhance the impervious ability and to prevent biological sulfuric acid from penetrating into the concrete, and to defer centralization of concrete and to prevent attenuation of its strength; The main purpose to enhance the anti- cracking ability is to control crack expansion caused by expansion of ettringite produced by the microbe erosion and to slow down the mass-transport process of the erosion medium and their products inside the concrete and decrease the invalidation speed of concrete.

The modification of concrete includes the choice of gelled materials, or the modification of polymer and reinforcement fiber. However, from a practical standpoint, the modification can only control the biological reaction dynamic process and retard the corrosion. Simple modifications will not be able to help release the corrosion process obviously, nor meet the practical requirement for the designed service life.

With coatings there are two kinds of counter measures for protecting concrete from microbe erosion. One is to use an inert coating which has anti-corrosion, impervious and anti-cracking abilities; another is to use a functional coating which has acid neutralization or bacteriostasis and sterilization function.

The inert coating can isolate concrete from contact with the biological sulfuric acid and can resist incidence of erosion. The acid resistant organic resin is adopted commonly. For example epoxy resin, polyester resin, urea formaldehyde resin, acrylic resin, polyvinyl chloride, polyethylene and asphalt etc., which have been reported largely in patents from China and abroad. Resin modified mortar as well as water glass coatings are other inert coatings.

To protect the coating from cracking, a reinforcing fiber is usually adopted, in which the epoxy coating can be modified with poly-sulfide to increase its adhesion and flexibility, as well it has also been reported that using compound coatings with epoxy resin, polyurethane foam as a bottom coating and with polyvinyl chloride, polyethylene as a surface coating.

However, all the above mentioned inert coatings have an obvious defect: firstly, all these coating materials are organism, which is not the same kind of material as the concrete substrate, and this will generate cracking, spalling and wear destruction; secondly, the application process is complex; thirdly, in these materials there are some components which are harmful to humans and to the environment; as well the cost of these materials are high.

The main purpose of a functional coating is to neutralize the biological sulfuric acid and/or restrain the production of the biological sulfuric acid, and to prevent the concrete from erosion. In fact, a neutralizing coating is a protective measure that sacrifices itself, by using an alkaline material as a protective coating applied on the concrete. This can neutralize biological sulfuric acid and enhance the pH value on the concrete surface, and consequently restrain the breeding of sulfur oxidizing bacteria.

The alkaline materials in common use are sodium carbonate, calcium oxide, magnesium oxide and magnesium hydroxide so on. Obviously these materials can be used only in easily accessible locations; and it can be expected that the application procedure is rather complex thus it will be difficult to carry out.

Summing up the above, currently, many projects urgently require highly efficient, safe and easy applied counter measures to protect concrete from microbe erosion.

If anti-corrosion, non-toxic, easy applicable and cost effective cementitious inorganic coating is adopted as "the inert coating," then all the above drawbacks brought by using organism can be excluded.

CN2000B (CCCW) Cementitious Capillary Crystalline Waterproofing Material made by ZHONGHE Waterproof Material Company Limited, is a "inert inorganic coating", which will integrate with the concrete substrate, and when in contact with water, it will produce a capillary crystalline and forms a dense, fast acting protective barrier which will protect from all the physical, chemical, biological erosions that are dependant on water as medium or carrier. This erosion process will not occur. At the same time, this material has a special composition that differs and makes it superior to other similar products from around the world.

Thus **CN2000B (CCCW**) not only has excellent waterproofing performance, but also excellent anti-corrosion performance that no other product can aspire to.

Because this coating has very low surface free energy or surface tension, it is not easily infiltrated with liquids such as acid solutions. Thus acid solutions have great difficulty in penetrating the coating and reacting with its compositions. In this coating material those free, to be able to be dissolving attacked, easy to be eroded compositions and one with low alkalinity decrease greatly, so the sensitivity of reaction with acid substance is lowered down; besides there is SO_4^{2-} in the molecular structures of hydrated products of **CN2000B**, so it has the ability to be resistant to the erosion of sulfate radicals. The testing by our company shows that this material can be used in the environment with a medium with pH≤3 for long term applications.

The National Research Council of Canada - Institute for Research in Construction has tested **CN2000B** according to the ASTM C-1202 standard for over 9 months. The study demonstrates this material has very good resistance to penetration of the chlorine ion. As it is known that the chlorine ion has a very small radius and a strong activity and has penetration and reactivity stronger than other acid radical ions, therefore, it can be said, the test also indirectly indicates that CN2000B has excellent performance to resist erosion of sulfate ions.

CN2000B has been used in many projects in environments similar to the above mentioned in domestic uses and overseas. For example the waterproof project of the Jizhuangzi Sewage Treatment Plant of Tianjin, the waterproof and impervious project of the Sewage Treatment Plant of Huainan city of Anhui province, the waterproof, impervious and plugging project of the Sewage Treatment plant in Qincheng District of Tianshui City of Gansu Province, the waterproof and leakage plugging project of the Sewage Treatment Pool of the Fuan Pharmacy Company of Chongqing, the waterproof project of the circulation waterworks of the SORALCHIN Sewage Treatment Plant of Algeria and the waterproof and impervious project of the adjustment pool of the life garbage disposal site of Hefei City of Anhui Province to mention a few.

Some of these have been used for 5 to 6 years since they were treated with **CN2000B**, and have performed superbly. The details of **CN2000B's** performance can be seen in the feedback opinions of our users.

In April, 2007 at the invitation of an American agency it was planned to do waterproofing and anticorrosion test on the underground pipe wall of Florida with **CN2000B**. The data about environment and the pipe system sketch can be seen in the attachment.

4. Conclusion

The destruction caused by sewage erosion to concrete sewage transport pipes is a serious problem which is faced by many countries of the world.

At first, engineers thought the corrosion was caused by hydrogen sulfide in the pipes.

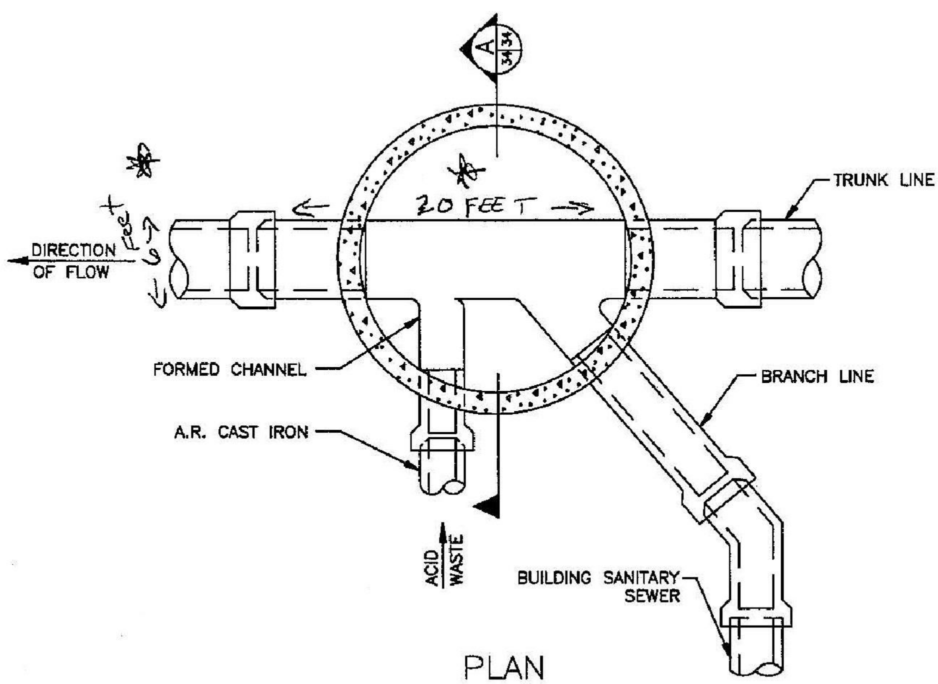
Intensive study showed that the substance of this erosion process is as follows: hydrogen sulfide is produced by biochemical action of bacteria and is acted under aerobe to oxidize to sulfur, which is oxidized again to sulfuric acid; it is sulfuric acid and other various inorganic and organic acids produced in the biochemical process that cause concrete on the wall neutralizing and lead CSH gelatin to decompose, and at last make concrete to destruct.

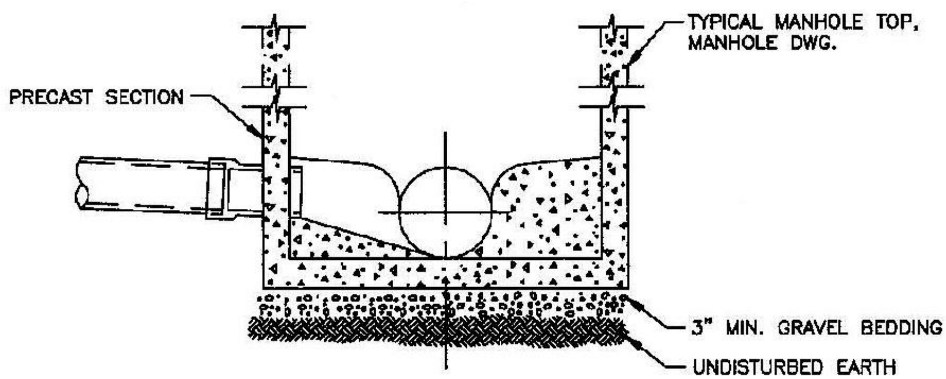
CN2000B (CCCW) Cementitious Capillary Crystalline Waterproofing Coating not only has excellent waterproofing and impervious performance, but also the special function of resistance to erosion of sulfuric acid and sulfates, which is none other than; this material has been used successfully in several sewage treatment projects in domestic and overseas. The practical projects have demonstrated: coating with **CN2000B** on the inner wall of sewage pipe is an economical, dependable and easy applied counter-measure for preventing and repairing pipe walls eroded by sewage.

Appendix

At the invitation of an America agency, in order to prevent seepage and resist microbe erosion to concrete we plan coating with **CN2000B** on the inner wall of sewage pipes in Florida. The data about the environment and the pipe sketch are as follows.

- Place: Florida
- Average temperature: 78 °F (25.6 °C)
- Humidity: 43 %
- Pressure: 30.15 in (765.81 mm Hg = 102.2 kPa)
- Dew point: 47°F (8.3°C)
- Testing area: Diameter 6 ft (1.829 mm); length 20 ft (6.096 mm). The total area of 10 pieces of pipe is 3770 ft^2 (350 m^2); the 3 ones in 10 pipes have holes.
- The pipe sketch:




TYPICAL MANHOLE TOP,
MANHOLE DWG.
PRECAST SECTION
3" MIN. GRAVEL BEDDING
UNDISTURBED EARTH

SECTION A