

# THE PROTECTION OF FLAT-ROLLED STEEL PRODUCTS FROM CORROSION IN STORAGE AND TRANSIT

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## **ABSTRACT**

In the packaging of flat-rolled steel products, the steel surfaces to be protected are in a nested configuration that specifies the operative corrosion mechanism. The characteristics of this type of corrosion are demonstrated empirically, and the controlling environmental parameters are discussed. Experimental data are presented as evidence that inhibitors can be used to control such processes.

Providing corrosion protection for sheet steel during its manufacture, during whatever storage is required, and while it is in transit to a customer's plant poses difficult problems for the steel producer. That is not to say that the technology necessary for dealing with these problems is not available. While the corrosion processes that give rise to these problems have been well understood in the corrosion science community for some time, corrosion specialists have not been very effective at imparting to the rest of the technical community, either an appreciation for what is required or the means to apply it.

The corrosion of a cold-rolled steel sheet surface requires that an aqueous electrolyte be in contact with that surface. No corrosion will occur, even at relative humidities approaching 100 percent, if the steel surface is free of contaminants, if the surrounding atmosphere is uncontaminated, and if condensation is avoided by keeping the temperature constant. Only the last of these conditions is met with any regularity under

our currently typical manufacturing conditions, and even this is lost when the steel leaves the manufacturing plant.

The role of hygroscopic surface contaminants in the atmospheric corrosion of sheet steel surfaces has been studied quite extensively for many years. Some 50 years ago, Vernon<sup>1</sup> detailed the connection between the absorption of atmospheric water vapor by contaminating inorganic salts and the corrosion rate of the contaminated steel surface. Many other workers have shown that at relative humidities well below 100 percent, salt particles on a steel surface will absorb water from the atmosphere and the resulting electrolyte can cause corrosion of the adjacent surface.<sup>2-8</sup> In this regard, a paper by L.E. Helwig<sup>9</sup> is particularly instructive. He set out to determine both the minimum level of chloride or sulfate contamination that would promote the rusting of steel during humid storage, and the highest relative humidity at which contaminated steel surfaces could be stored without rusting. From this work he concluded that a chloride contamination of as little as 0.4 mg/m<sup>2</sup> (0.037 mg/ft<sup>2</sup>) would cause rusting at relative humidities greater than approximately 30 percent. For sulfates, he found that a contamination of 0.7 mg/m<sup>2</sup> (0.065 mg/ft<sup>2</sup>) will promote rusting at relative humidity greater than approximately 55 percent. He also showed that the critical relative humidity for the rusting of contaminated steel surfaces is determined by the hygroscopicity of the ferric chloride or ferric sulfate formed on the steel surface by reaction with the contaminating salt.

It should be noted that the limiting values given above describe the conditions necessary for the initiation of a corrosion process. Clearly, the rate at which such a process subsequently proceeds will increase markedly with an increase in the amount of contamination present or with a rise in the relative humidity. Accordingly, anything that can be done to lower the level of contamination on the surface, or to lower the relative humidity of the atmospheric environment in contact with that surface will lower both the probability of corrosion occurring and the extent to which it does so.

The fact that sheet steel is normally processed in coil form presents additional problems to the steel producer because of the “nesting” configuration assumed by steel surfaces in a coil. In the manufacturing plant, the most important consequence of this configuration is that the surfaces of interest are virtually inaccessible during a critical period in the processing sequence. Steel producers agree that in-plant rusting occurs primarily on freshly annealed coils while they are awaiting temper rolling. The problem is largely limited to the summer months when relative humidities are high, and is generally in the form of pinpoints of rust, approximately 5 mm in diameter, which are widely and randomly scattered. The incidence of such rusting increases dramatically with increasing length of the storage time between annealing and temper rolling. Steel

producers should, therefore, minimize the length of this storage period and should, as a rule of thumb, avoid allowing it to exceed five days.

It is generally believed that such rusting is caused by a contamination of the sheet surface that takes place during the processing that precedes annealing. This view is supported by several studies that have indicated that pinpoint rusting is attributable to surface contaminants that survive the annealing process and promote rusting during subsequent storage.<sup>10-12</sup> It should be noted that the minimum level of contamination that will produce rusting under humid conditions is so low that it is difficult to avoid exceeding under the best of our manufacturing conditions as they currently exist. However, our normal production history provides evidence that, with careful attention to processing details, the incidence of in-plant rusting can be kept to a low level. Clearly, any processing lapse that results in more contamination will greatly exacerbate the situation. Such a lapse might involve inadequate rinsing on a continuous pickle line or the inadvertent introduction of contaminants on a tandem mill or wash line. Pinpoint rust, or as it is sometimes called, "speckled rust," consists of tiny spots of rust that are widely scattered and randomly distributed. Rust that is attributable to a processing lapse will display a linearity, or a periodicity, or some other pattern that will clearly distinguish it from speckled rust.

In the steel industry, the traditional way of providing protection from corrosion that might occur in storage or during shipment has been to apply great quantities of oil to sheet surfaces, and then to bolster that with still more oil applied to the exterior surfaces of coils. Prior to temper rolling, sheet surfaces are not accessible for the application of oil, or any other full surface treatment. The problem of providing corrosion protection prior to temper rolling is similar to that encountered in the case of steel which, for one reason or another, must be shipped in the dry condition. It is important to note that until relatively recently, no suitable technique for providing such protection was available. This is the application for which vapor phase inhibitors are starting to be used.

Vapor phase corrosion inhibitor technology is not new. Over a hundred years ago it was common practice to place a piece of camphor in a gun cabinet to keep gun barrels from corroding. The systematic development of new and more effective vapor phase corrosion inhibitors, however, dates from World War II. The necessity for protecting military equipment and the associated replacement parts from corrosion in storage provided the impetus for the development of such products. Among the more successful of the materials developed during this period were the nitrite salts of various organic amines. One of these in particular, dicyclohexyl ammonium nitrite, often referred to as dichan, has been quite widely used. There has also been a great deal of interest in the development and use of vapor phase corrosion inhibitors in other countries.<sup>(13)</sup>

The alkali metal salts of several inorganic acids have long been known as effective corrosion inhibitors for ferrous alloys in aqueous solution. Sodium nitrite and sodium chromate, for instance, have been widely used for many years. The organic amine salts of such acids have similarly been shown to be effective in aqueous media, but in contrast to

the alkali metal salts, many of the corresponding solid amine salts are slightly volatile at atmospheric temperatures. This property is especially important to the steel industry because it makes possible the protection of steel products whose corrosion susceptible surfaces would otherwise not be readily accessible.

The corrosion that takes place within a coil during in-plant storage is, as indicated earlier, the result of water vapor diffusing into interstitial spaces within the coil and being absorbed by contaminating inorganic salts on the steel surface. Any pathway available to water vapor would also be available to inhibitor vapors. Thus, the property of volatility provides a method of transport to those areas on the steel surface that require protection. Such a corrosion inhibitor, applied to the exposed lap edges of a steel coil, does not function by forming a barrier to keep water vapor out of the interior of a coil. Rather, it prevents the corrosion of a steel surface when an electrolyte is present.

Some 10 years ago, we demonstrated, both in laboratory simulation tests and in actual mill trails, that when dicyclohexyl ammonium nitrite dissolved in methanol was sprayed onto the exposed lap edges of dry coils, corrosion during subsequent humid storage was effectively prevented. The methanol carrier volatilized during the application leaving a light dusting of the solid inhibitor evenly distributed on the exposed lap edges. Treating only the exposed lap edges of coils minimized the probability that the presence of corrosion inhibitor on interior surfaces would affect subsequent processing. Industrial hygiene considerations, however, discouraged the use of methanol. Although also shown to be effective, the direct application of corrosion inhibitor powder to coil edges was discouraged on similar grounds. Concern was also voiced that organic nitrites might be converted into nitrosamines and thus produce potentially carcinogenic materials.

A few years ago products began to appear in the market place that seemed to address these difficulties. The carrier used was water and the corrosion inhibitors themselves consisted of materials that were more acceptable on industrial hygiene grounds. The use of water as a carrier caused some concern as this raised the question of possible transport competition between water vapor and inhibitor vapors. The exposed panel edges of a stack of cold-rolled steel specimens were sprayed with an aqueous solution of one of these inhibitors. The stack consisted of 25 panels and was tightly bound with the same strapping material used commercially to band coils. It was then subjected, along with an untreated but otherwise similar control stack, to an environment in which the relative humidity was maintained at 100 percent, and in which the temperature was cycled between 49°C and room temperature to ensure that the test specimens would be exposed to severe condensation. The length of exposure was determined by how long it took to develop unequivocal evidence of corrosion on the control stack. This laboratory test, since repeated many times, demonstrated that cold-rolled steel is, by such an edge treatment, effectively protected from corroding in a condensing environment. These laboratory results have been corroborated on a commercial scale.

From the earliest mill trails, the method of applying edge treatments was found to be critical. It is essential that complete coverage of the coil edges be achieved, although a

light application of that complete coverage will suffice to provide the desired protection. Another important concern in the application of such edge treatments, is that the corrosion inhibitor not penetrate between coil laps. Inhibitor on a strip surface can cause difficulties if that material is transferred to mill rolls, and it can also interfere with subsequent processing of the surface. Another reason for minimizing the amount of inhibitor solution applied is that a heavy application enhances the probability of forcing the water carrier in liquid form between the laps; this can interfere with the effective functioning of the corrosion inhibitor. In many cases, an airless spray device provides a suitable application technique for such an edge treatment. It has been demonstrated, for instance, that it is possible to dry temper roll steel with no problem whatsoever after treatment in this fashion. Where subsequent processing requirements make it especially important to avoid inhibitor penetration between coil laps, it is possible to limit penetration to approximately 0.5 centimeter using an electrostatic application device.

There is another form of storage and transit corrosion known as storage stain that is familiar to steel producers. It results from liquid water coming into contact with the steel surface. When water condenses on the exposed lap edges of a coil as the result of a drop in temperature, it can be drawn between the laps by capillary action and produce a black stain. The corrosion product in this case is a black magnetite, rather than the more completely oxidized red ferric oxide, because the supply of oxygen available for reaction within the coil is limited.

Although oiling a sheet surface can be quite effective in preventing storage stain, it has been found to be less than completely protective in the prevention of rust that is attributable to surface contaminants. This has been documented by some German workers<sup>14</sup> among others, and is especially true if the contamination is appreciable and if the environmental exposure is particularly severe or of uncommonly long duration. Imperfect oiling that leaves dry spots or streaks on the sheet surface will make the situation much worse. In this connection, the relatively recent introduction of electrostatic oiling devices represents a significant improvement in processing technology. Oil-soluble corrosion inhibitors, which have been incorporated in shipping oils for some time, are also continually being improved and are accordingly providing increasingly more effective corrosion protection.

Water-soluble corrosion inhibitors designed for use in a full-surface application have also become available in recent years. These materials contain surfactants which make it possible for the steel surface to be completely wetted by a water solution. Such treatments are intended to replace the customary oiling done by steel producers. There are compelling reasons for contemplating this change.

- A) Corrosion resistance can be significantly improved,
- B) Cleaning of the steel surface prior to subsequent processing is greatly facilitated,
- C) Plant housekeeping for both the producer and the customer is simplified, and

- D) Lubricity to assist metal forming operations can be superior to that provided by shipping oil.

In considering the corrosion of flat-rolled steel products in storage or in transit, it has been noted that there are five steps that can be taken to avoid its occurrence:

- 1) Minimize contamination of the surface,
- 2) Control the temperature to avoid condensation,
- 3) Control the humidity of the atmospheric environment,
- 4) Prevent exposure of the surface to a contaminated atmospheric environment, and
- 5) Apply corrosion inhibitors judiciously.

Reviewing the processing sequence, one can note the opportunities for applying each of these corrosion control steps. First, an effective rinsing of the steel surface after pickling is critical. In this connection, it is not sufficient to neutralize the pickling acid; the salts that result from this neutralization must also be removed. Every exposure to water of the sheet surface prior to annealing is a potential source of inorganic contaminants. Care must be taken in each instance to minimize such contamination. Corrosion inhibitors could be applied at the end of any or each of the processing steps but the protection would likely be lost at the very next step. It is generally accepted that the commonly available corrosion inhibitors are destroyed under annealing conditions. Kolts<sup>15</sup> described an interesting process designed to eliminate contaminating surface chlorides during the annealing process. It consists of rinsing the surface with a phosphate solution at the tandem mill, and it is claimed that the contaminating chlorides are converted by reaction with the phosphate into a foam that volatilizes during the box anneal.

The use of modern electrolytic cleaning techniques after tandem rolling could certainly go a long way toward minimizing inorganic contaminants on a sheet surface.

After annealing, the hot coils are usually allowed to cool on the mill floor where humid air is drawn into the coil interiors as the coils lose temperature. Following a procedure first suggested by Evans and Taylor,<sup>16</sup> some Japanese sheet mills force-cool freshly annealed coils to room temperature with air that has been dehumidified using lithium chloride to a relative humidity less than 25 percent.

The edge treatment of freshly annealed coils with a vapor phase corrosion inhibitor applied electrostatically has been described in some detail. For steel that is to be shipped dry, the edge treatment can be repeated after temper rolling.

If steel is to be stored for any length of time after rolling, it is important that the steel be wrapped or at least covered as soon as possible. The settling of atmospheric contaminants on the exteriors of coils is the prime cause of edge rust. Storage areas where both the temperature and the humidity are controlled would be most desirable but would also be prohibitively expensive for most steel producers.

For protection from transit corrosion, a full-surface treatment either with a suitable water-based corrosion inhibitor or with a shipping oil that contains an effective inhibitor will serve the purpose.

In summary, no corrosion will occur, even at relative humidities approaching 100 percent, if the steel surface is free of contaminants, if the surrounding atmosphere is uncontaminated, and if condensation is avoided by keeping the temperature constant. Since the meeting of these three criteria in the commercial environment is very difficult if not impossible, a judicious use of appropriate corrosion inhibitors is recommended as a supplemental measure.

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## **PROTECTION OF STORAGE TANK BOTTOMS USING VOLATILE CORROSION INHIBITORS (VCI)**

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### **SYNOPSIS**

Storage tank bottoms have historically been protected from corrosion using Cathodic Protection (CP) in general, this has worked well. Problems arise when there is not complete contact with the base. This occurs as the bottom “works” with filling and emptying of the tank. The bottom buckles slightly, leaving air gaps. Other times a portion of the base may erode. In either case, electrical continuity is lost. Other methods of protection such as protective coatings are not suitable. When the bottom plates are welded together, the welding destroys the coating.

Research and field work show that protection can be achieved using Volatile Corrosion Inhibitors (VCIs) under the tank. This works alone or in combination with CP.

Double tank bottoms for leakage monitoring are often specified for new tanks. The same problem as above occurs. VCI's are an excellent solution from both a technical and economic standpoint. These inhibitors have a long history of corrosion protection under these types of conditions (wet, corrosive environments and void spaces). Chemistry testing, and case histories will be presented.

## **INTRODUCTION**

Steel tanks have been with us for about the last 100 years. Prior to this tanks of masonry and wood were common. These materials had some good properties, but steel became the material of choice for many reasons--it is modular, easy to configure in many shapes and sizes, easier to make "leak tight" and is economical for most uses. In some cases, virtually no corrosion protection system is necessary (1).

Where necessary, exterior corrosion control of the sides and top is easily achieved by painting. Internal protection is unnecessary with many products (petroleum, many organic chemicals, gases, etc.). When required, linings or CP provide good protection.

The underside in contact with soil is a more difficult situation. Coatings can not be applied, as welding of the plates destroys the coating integrity. There is no way to reapply the coating in the welded areas. If there is perfect contact with the soil or base, CP works well. However, Life is not perfect. The bottom buckles from "working" of the tank, filling and emptying. Welding stresses warp the plate slightly. The sub-base material may shift, settle, or get washed out. Leaking petroleum compounds can change the conductivity of the soil.

## **CORROSION**

If corrosion of the bottom were general, a suitable corrosion allowance could be built in. However, often a pitting corrosion is seen, where holes are literally drilled through thick steel plate.

In the past, minor product leakage was accepted. The cost of the product lost was not always great enough to be a major concern. With recent environmental regulations, leakage is a major concern. Vast amounts of groundwater can be contaminated. The cost of cleaning up this pollution can amount to millions of dollars. In extreme cases, the site is not salable on the open market. Most companies want to present a favorable public image. Leaking tanks destroy this image very rapidly.

Newer tanks are designed with secondary containment. There are double bottoms for leakage detection, and concrete or membrane containments to limit product migration if the product escapes the tank.

Figure 1--oil storage tank, membrane, ringwall, double bottom

## **CORROSION PROTECTION**

Even with the detection and collection systems, corrosion protection still needs to be addressed.

**Vapor Corrosion Inhibitors (VCI)** have been used for many years to solve the basic problem of protection of metal surfaces in a confined space. An early use was Shell Chemical's VPI, (Vapor Phase Inhibitor) used as early as World War II. They did work, but the problem was toxicity of organic nitrites.

VCI's are a sub-class of metal inhibitors. Inhibitors have been used by the oil and chemical industry for over 50 years, minimizing difficult corrosion problems. This is well documented in the literature as well as by use in the market place. A unique characteristic of VCI is its relatively high vapor pressure (.0001 mm Hg). These inhibitors volatilize at room temperature, redepositing on metallic (as well as other) surfaces in an equilibrium condition in confined spaces. The inhibitor then functions as any other inhibitor, stopping or retarding the corrosion mechanism. They are chem-adsorbed in a 2-3 thick molecular layer. Some compounds are specific for ferrous metals, other are effective on both ferrous and non-ferrous metals.

In the last twenty years several companies investigated these compounds and developed a series of low toxicity (2), many being in the range of table salt, 2000-3000 mg/Kg oral LD-50. A key characteristic of these materials is that they protect against corrosion in the presence of water vapor, chlorides, hydrogen sulfide, sulfur dioxide, nitrogen oxides, and other compounds found in a corrosive industrial environment.

These newer VCI's are being used daily for successful protection. They are produced and used in many forms: pure VCI powder, VCI liquids, "emitters" used in electrical and electronic applications, VCI plastic films and paper used in packaging, lubricating oil/VCI combinations, and incorporated into standard solvent and water based paint formulations. These materials have been incorporated into standard specifications by companies such as Dupont, Conoco Oil, IBM, Motorola, General Motors, Ford, Chrysler, and Volkswagen. Organizations such as the United States Navy use this type of protection, saving vast amounts of money compared to previous preservation methods. The US Navy has an active program evaluating several VCI's for use in void spaces in ships (3).

## **APPLICATION TO TANK BOTTOM PROTECTION**

Several years ago Conoco Oil recognized the tank bottom problem and published a paper (3) presenting laboratory testing procedures and showing very positive results. A given quantity of VCI was mixed with a given volume of sand/gravel mix, and corrosion monitored over a two year period. Real world experience of VCI's in void space protection over a 15 year time span has confirmed for a long time the effectiveness of this approach.

This type of protection is incorporated into standards for protection of tank bottoms, new and existing. It has also been incorporated into the void space of double tank bottoms.

## **TANK BOTTOMS**

## 1. NEW TANKS

After the sub-base of sand/gravel is spread, VCI powder is applied at the rate of 1-2 Kg/100 square meters (2-4 pounds/100 square feet). It is mixed into the base with simple hand tools. The tank bottom is then laid out and fabricated as normal. The VCI slowly distributes itself uniformly throughout the base. At welds a small amount vaporizes, but recondenses after cooling of the metal.

In the case of a concrete base, VCI is applied to the surface, or a modified form is mixed into the wet concrete. Migration of this inhibitor has been extensively evaluated by several organizations (5,6).

## 2. EXISTING TANKS

When tanks are being refurbished and new bottom plates are welded in, VCI's are spread under the plate. When possible, VCI's are distributed in the adjacent areas as best possible.

VCI's may also be placed by air lancing under existing tanks from the perimeter, and blowing the powder in during the withdrawal process. Ashland Oil recently completed an evaluation in Pittsburgh using this process, then analyzing the base for distribution after removal of floor plates.

## **DOUBLE TANK BOTTOM PROTECTION**

(Figure 2 & 3)

### 1. NEW INSTALLATIONS:

After the 1st bottom is installed, VCI powder is spread at the rate of 1-2 Kg/10 square meters (2-4 pounds/100 sq. ft.). The spacer and second bottom is then welded in place.

### 2. EXISTING INSTALLATIONS

VCI powder is blown into the void, taking care to provide uniform distribution. Alternately, a VCI solution may be pumped into the void, and either left or drained. Either method provides corrosion protection.

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## **CONCLUSIONS AND COMMENTS**

Years of experience have shown that VCI's are very effective in preventing corrosion. Common questions are:

1. How do we know these inhibitors work in the presence of CP? Years ago the Alyeska pipeline in Alaska/Canada experienced a major corrosion problem with the exterior of their epoxy coated pipeline when groundwater penetrated the insulation jacket. A VCI inhibitor was injected into the saturated insulation. This was monitored for corrosion activity and concentration over a 10 year period. CP was also used at the same time. At the end of 10 years, corrosion protection still remained, and over 85% of the original inhibitor was left (7). These compounds generally are quite stable.

2. How do we evaluate the effectiveness? Corrosion protection can be monitored using corrosion probes similar to those used in pipelines (8). Reapplication of inhibitor may be necessary at 5 or 10 year periods, but if the base is reasonably well sealed, reapplication may not be necessary.

## **CONCLUSION**

VCI's have proved their effectiveness over many years. The use as a protection for the underside of steel tank bottoms and void spaces of double tank bottoms solves the corrosion problem in a time proven manner. The application is relatively simple. It has also proven to be an inexpensive procedure as well.

FIGURE 1:

SCHEMATIC OF METAL SURFACE

Structure of a "Typical Surface"

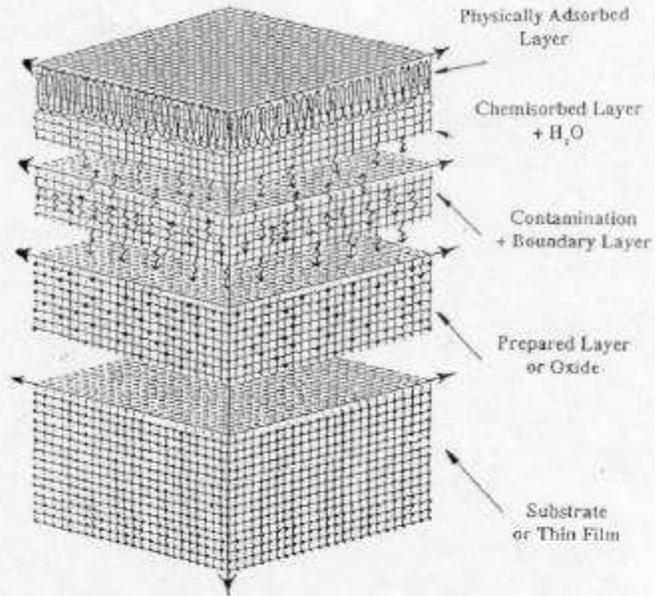
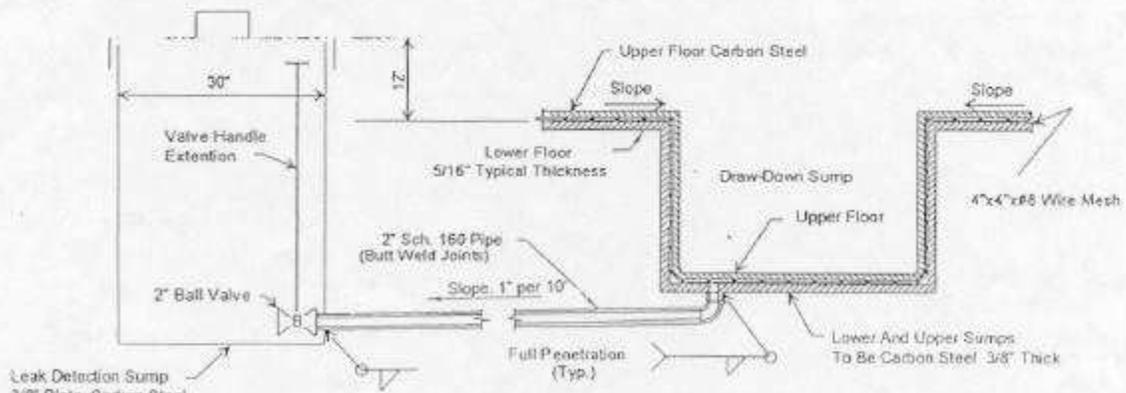


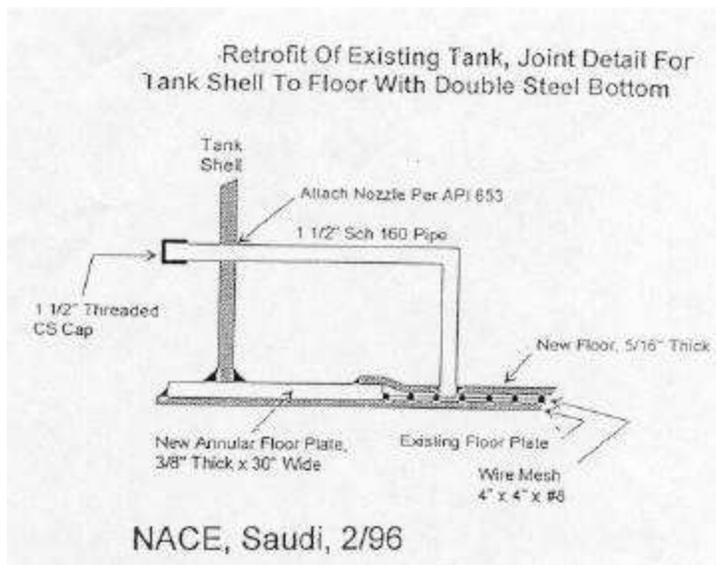
FIGURE 2:

DOUBLE TANK BOTTOM

Double Steel Floor Design With Gravity Drain-New Tanks



- Note:
1. Upper & Lower Tank Sumps, External Witness Sumps and Leak Detection Piping Should Be Installed By Foundation Contractor.
  2. Drain pipe from sump can be installed above floors to tank shell per Figure 4



**FIGURE 3: RETROFIT OF TANK BOTTOM**

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