METALLOID COATING TEST PROGRAM FOR SUCKER RODS IN CORROSIVE WELLS

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ABSTRACT

A coating process is under development for protecting downhole tools and components with a proprietary Al_2O_3 based metalloid coating that appears to provide a barrier to many forms of corrosion attack. Laboratory NACE TM-01-77 tests results performed at Battelle and NMTU laboratories resulted in no “720 hour failures” or “indefinite time to failure” due to corrosion damage. Comparable uncoated specimens failed in less than five hours. Subsequently, coated pony sucker rods were installed in a West Texas well with aggressive H_2S and CO_2 fluids and pulled after 5 months in service. This paper will provide a review of the laboratory test results and a post-pull analysis of those pony rods relative to other uncoated sucker rods from the same wells.

INTRODUCTION

On March 14, 2003, the authors met with New Mexico Tech University (Socorro) and planned a program to test several downhole components in high CO_2 and H_2S service, in wells in West Texas where severe corrosion damage is common. The original laboratory and field program was funded by U.S. Department of Energy and Space Alliance Technology Outreach Program.

The primary task of this project was to determine how the coated tools responded to ordinary handling at the well site; the subsequent protection offered to corrosion attack from high H_2S and CO_2 containing fluids and to compare these results to adjacent bare components installed in the same well at the same time. The coated parts were tested in one selected well in the production area in West Texas with high concentrations of the acid gases.

Four 7/8” X 2 ft, and three ¾” x 2 ft UHS pony rods and twelve 2-7/8” X 6 inch pipe nipples were prepared by cleaning and sand blasting the surfaces. Then a metalloid coating is applied. Initially, the metalloid coating thickness was about 0.020 in. and about 0.007 inch after processing. Not all the original coating thickness is converted to the protective coating and a portion is left on the surface and is anodic to any exposed steel. The pipe nipples were coated on the inside surface.

Three of the 7/8” pony rods were successfully installed and removed for examination. They were installed in a waterflood San Andres well and they experienced the severe corrosive environment desired. Two 3/4” pony rods were installed in a waterflood Clearfork well, where they operated for over one year, but the perceived challenge of that well did not manifest itself, as the well was later found to have little H_2S and CO_2. These second two pony rods suffered almost no degradation. Two pipe nipples were installed in another well’s tubing string, but they became “lost” in the difficult-to-control circumstances of every day oil field well servicing.

This paper will discuss the corrosion process, the metalloid coating, laboratory testing of steel samples and results of that study and the test pony rods installed and removed from the San Andes well called here in as Well 697.

WHAT IS CORROSION?

Corrosion, the degradation or deterioration caused by chemical reaction with the environment, affects materials as different as structural metals, ceramics, and wood, as well as works of art and artifacts from past civilizations. Corrosion technology is a field of study that focuses on the mechanisms of corrosion and on the design of protective schemes to prevent it or limit its extent of metallic material from corrosive environment

Most corrosive-susceptible steels corrode because of the release of stored energy in the material from manufacturing process, and secondly, the material is returning to its most stable or natural state, i.e., oxides, carbonates or other compounds.

ACID GAS CORROSION AND STRESS CRACKING

Produced water containing acid gas is the most common form of corrosion in an oilfield and includes hydrogen sulfide (H_2S) and/or carbon dioxide (CO_2) and forms general areas of corrosion and deep, isolated, and randomly scattered pits, localized areas of deep, sharp-sided pits adjacent to areas of little corrosion. Other forms are: hydrogen embrittlement [HE] is frequently found in oilfield equipment and piping. HE occurs in high strength steels in wet sulfide systems and water forms weak acid causing sudden, unexpected failures to occur. The absorption of hydrogen causes a loss of ductility in steel and fracture surfaces display brittle or granular appearance. Hydrogen-induced cracking [HIC – see Fig 1] and blistering can occur in lower-strength steels if partial pressures are high enough. Other forms of downhole corrosion reactions occur from hydrogen sulfide, carbonic acid, bacteria corrosion, oxygen reactions and brines (salts).

NACE TM 01-77 SCC TESTS

The Stress Corrosion Cracking (SCC) test program, usually a test for steel alloy's resistance to SCC, was conducted prior to the field testing by Battelle Labs in Columbus, Ohio and the NMTU Metallurgy Department laboratory in Socorro, New Mexico. The purpose of these tests is to determine the susceptibility to corrosion cracking of components regularly made with materials listed in NACE MR 01-75. The autoclave, shown in Figure 2, requires a simulated downhole environments with a pH of 3.5 including bubbling H_2S through the fluid, the expected temperature range, applied tension load to stress the sub-sized tensile bar sample to 99 % of its yield strength and time. Test duration of 720 hours without failure of the test sample is considered to be resistant to SCC under these simulated downhole conditions.

Laboratory conditions of hardened steel specimens, stressed to 96% of the yield strength. The Battelle test samples were made from one steel alloy, AISI 4130, heat treated to two yield strength levels, 88,000 psi and 104,000 psi. All samples were coated with the metalloid [ceramic like] material to about 5 mills. The NMTU samples were made with two steel alloys, AISI 4140, heat treated to 112,000 psi and AISI 1045, heat treated to 120,000 psi. Two samples of each alloy were coated with the metalloid. The laboratory tests from both labs are shown in Tables 1 – 3.

The NMTU test results are also depicted graphically in Graphs 1 and 2. The uncoated samples failed, while the coated samples (depicted by the blue dashed lines) did not.

FIELD TEST

The primary task of this project was to determine coating response to ordinary handling at the well site; the subsequent protection offered to attack from high CO_2 and H_2S containing fluids and to compare to adjacent bare components installed in the same well at the same time.

Originally, seven 7/8" x 2 ft. ultra high strength case hardened pony rods and twelve J-55 2-7/8" x 6 inch pipe nipples were prepared by cleaning, sand blasting and coating the surface. The initial metalloid coating thickness was about 0.020 in. and about 0.007 inch after processing. Most of the coating is converted to the protective coating and a portion is left on the surface as a metallic compound anodic to steel.

Two 7/8" pony rods were tested in Well 697. This well is located south of Penwell, Texas, in an area known as The Sandhills. In early 2002, Well 697 was recompleted to a waterflooded San Andres zone, and was hydraulically sand fractured during that process. The depth to the well's seating nipple is 3354 feet. Since recompletion, this well has suffered 3 tubing and 3 rod failures where in corrosion was the primary source of failure and forced the near complete replacement of 4 rod strings and 3 tubing strings. The well operated with a high fluid level until larger lift equipment could be installed. Later the well was equipped with polyethylene lined tubing to help mitigate tubing failures and fiberglass rods to reduce rod failure frequencies. A 2004 well head sample of produced water was found containing over 260 mg/L CO_2 and 599 mg/L H_2S in solution, while the field free gas contains about 1.8 mole % CO_2 and 1.5 mole % H_2S.

The coated 7/8" pony rods were installed on Dec 22, 2003, they were placed under the polished rod and used to space the rod pump plunger. They were subjected to as much loading pressure as any other rod in the well. Later, they were pulled from the well on May 6, 2004 to be studied. Both dates mark well service events where in corrosion related failure had occurred. Along with the pony rods a sample of one of he UHS uncoated sucker rod about four feet long was acquired. (The rest of the rod string was junked due to pitting.)

The pony rods were cleaned and found to be intact, no pitting. The bare rod had suffered from corrosion, and spalling. The spalling pattern was along a wear line, but main cause of metal loss was spalling of the hard outer layer. The outer layer of the ultra high strength sucker rod is heat treated by induction during manufacturing and this process hardens the outer surface to about 50 HRC whereas the core hardness is usually about 30 HRC. This process forms a compressive case about 0.050 in thick. Visual inspection of the surface shows rod failure caused by very heavy corrosion damage. It appears that corrosion activity caused hydrogen embittlement of the hardened case and subsequently caused spalling, greatly compromising rod string integrity. See Photos 3, 4, and 5.

Two ¾" pony rods were in the Clearfork well for over 1 year, and was removed during a pump job. That well did not have the corrosion anticipated, and later it was realized the well produced fluids have very little acid gas in them. A photo of one of rods, cut in half for the photo: one end showing oxidized FeS scale still on it, and one end "shot" peened to expose the metalloid underlying the scale. Note the "silvery" glean.

CONCLUSIONS

In conclusion, the very positive and encouraging test results from the laboratory and field test program done so far. The coating does appear to prevent hydrogen induced cracking and spalling of ultra high strength steels without loosing the tensile strength properties of the steel.

Plans are underway to coat steel pin-ends of a fiberglass sucker rod string in another well similar to Well 697. Another test, if as successful as the ones so far, will definitively point this program in the right direction and begin the final development of coating the inside surface of oil country tubular products. It is very much projected this coating will provide excellent corrosion protection and resist very tough handling at high temperatures at a very competitive price.

ACKNOWLEDGEMENTS

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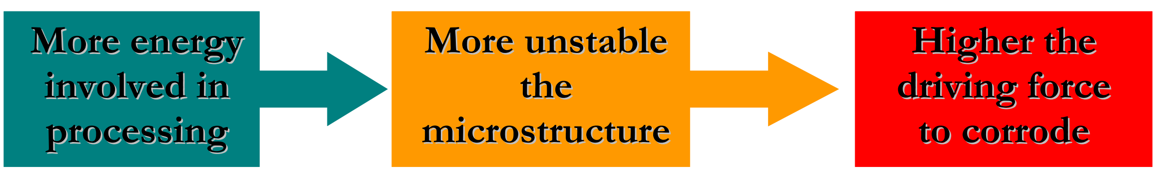


How aggressive is your corrosion?

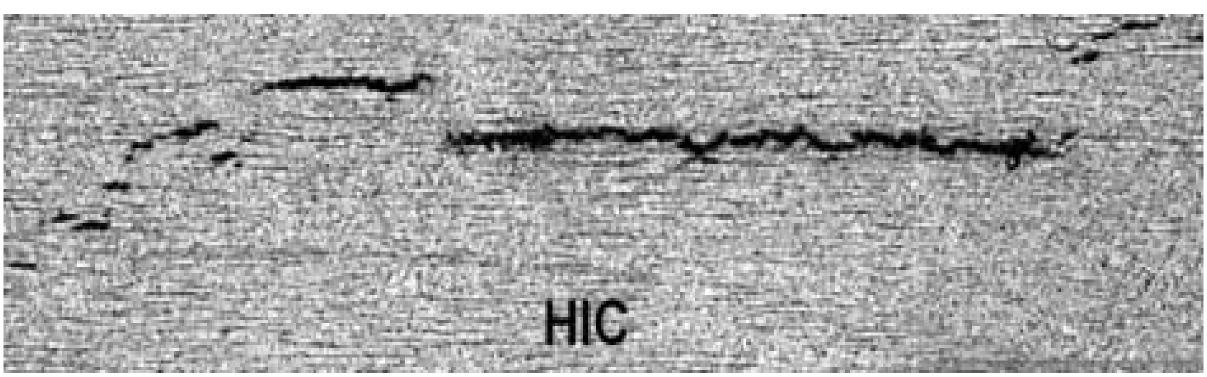


Figure 1- Photomicrograph of Hydrogen Induced Cracking [HIC] and stepwise cracking caused by hydrogen embrittlement [HE].

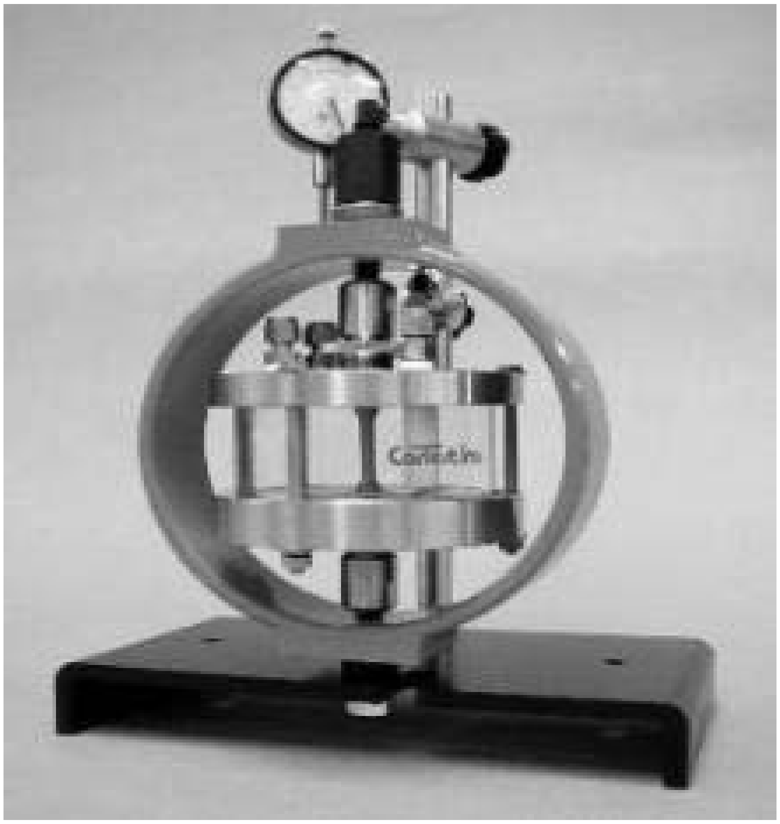


Figure 2- TM01-77 Test Apparatus

Laboratory Testing

Table 1
Battelle Test Results: Sample N3 was mistakenly tested at 62% then increased to 81.9% but did not fail. Sample N6 failed prematurely due to a defect in the tensile bar.

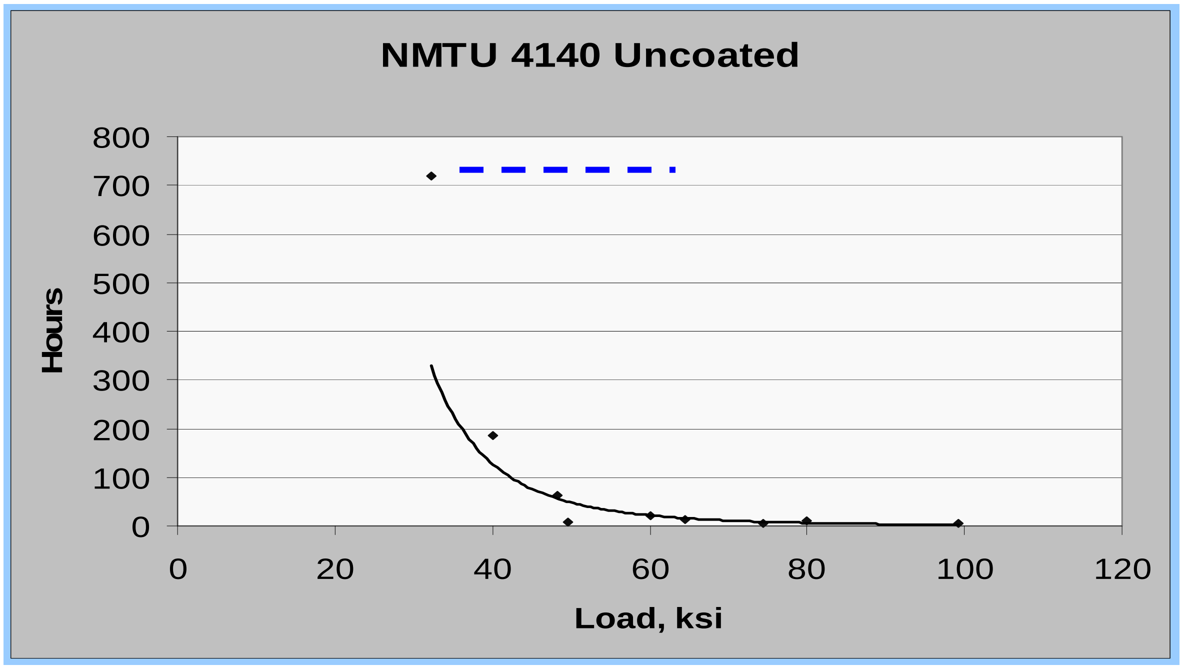
Coated	Specimen	Load, ksi	Hours	Fail--NFail	Remarks
AISI 4130	N1	42.5	720	NF	Yield 88,000 psi
	N2	53.2	720	NF	
	N4	71.2	720	NF	
	N5	79.2	720	NF	
	N3	62/81.9	720	NF*	424hrs/720 hrs
	N6			Fail*	Sample Defect
AISI 4130	U1	51.4	720	NF	Yield 104,000 psi
	U2	65.1	720	NF	
	U4	78	720	NF	
	U5	94	720	NF	
	U3	98.2	720	NF	
	U6	102.9	720	NF	

Table 2
NMTU SCC Test Samples: Samples were either tested as received, normalized or quenched and tempered.

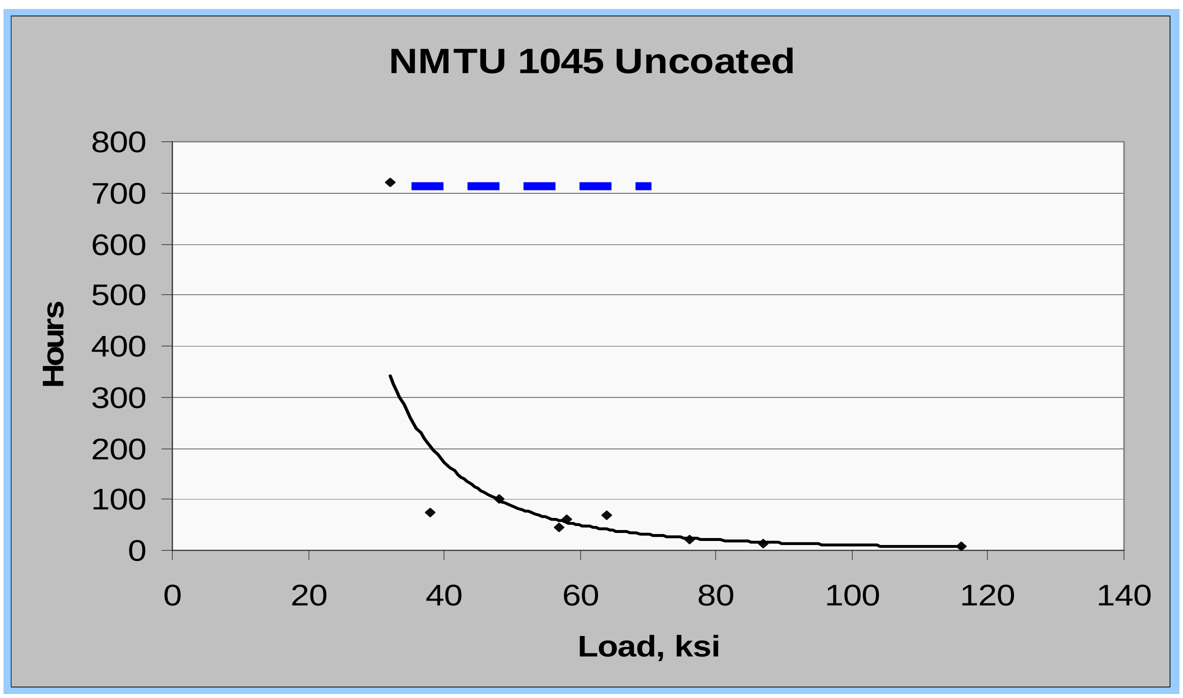
4140	*Condition*	*Austen F*	*Temper F*	*Yield ksi*	*Tensile ksi*	*HRC*
1	**As Received**	**Cold Drawn**	**none**	**120**	**144**	**33**
2	**Normalized**	**1600**	**air**	**100**	**140**	**32**
2.1	**Norm+Coated**	**1600**	**1325**	**72**	**99**	**27**
3	**Q + T**	**1560 oil**	**1000**	**124**	**131**	**32**
3.1	**Q + T (coated)**	**1560 oil**	**1325**	**99**	**112**	**29**
4	**Q + T**	**1560 oil**	**1150**	**100**	**109**	**29**
5	**Q + T**	**1560 oil**	**1300**	**81**	**90**	**20**
1045						
1	**As Received**	**Cold Drawn**	**none**	**90**	**110**	**22**
2	**Normalized**	**1600**	**air**	**80**	**91**	**18**
2.1	**Norm+Coated**	**1600**	**1325**	**52**	**76**	**15**
3	**Q + T**	**1550 water**	**1000**	**145**	**155**	**34**
3.1	**Q + T (coated)**	**1550 w**	**1325**	**115**	**120**	**31**
4	**Q + T**	**1550 w**	**1150**	**95**	**115**	**26**
5	**Q + T**	**1550 w**	**1300**	**80**	**90**	**19**

Table 3 - NMTU TM 01-77 Test Results. Comparing the normalized or the quenched and tempered samples for each uncoated and coated samples, the uncoated samples failed within 7 hours at loads of 54,000 lbs and 99,000 lbs. Coated samples 2.1 and 3.1 were compared to equivalent uncoated samples tested at about the same loads. Coated sample 2.1 did not fail but was stopped after 400 hundred hours.

Sample No.		**4140**			**1045**	
(Chart No.)	**%Stress (Y)**	**Load, ksi**	**Fail, Hrs**	**%Stress (Y)**	**Load, ksi**	**Fail, Hrs**
1 CD	80	96	2	80	72	2
1 CD	60	72	3	60 (80)	54	4
1 CD	40	48	7	40	36	8
2 Nor	80(100)	80	5	80	64	9
2 Nor	60	60	11	60	48	18
2 Nor	40	40	20	40	32	31
2.1 coated-Nor	115(72)	83	60*	104(52)	54	400NF*
3 Q+T	80(100)	99.2	4.5	80	116	7
3 Q+T	60	74.4	6	60	87	14
3 Q+T	40	49.6	9	40	58	62
3.1 coated, Q+T	98(99)	97	720NF	98(115)	112	720NF
4 Q+T	80	80	9.5	80	76	22
4 Q+T	60	60	22	60	57	45
4 Q+T	40	40	185	40	38	75
5 Q+T	80	64.4	12	80	64	70
5 Q+T	60	48.3	63	60	48	100NF
5 Q+T	40	32.2	400NF	40	32	200NF



Graph 1 - NMTU TM01-77 Test Results: Test results for the 4140 samples show an immediate degradation of strength shortly after loading. No coated samples failed [blue dashed line].



Graph 2 - NMTU TM01-77 Test Results: Test results for the 1045 samples show an immediate degradation of strength shortly after loading. No coated samples failed [blue dashed line].

Figure 3 – Samples from field test. Beginning at lower left to right: 2 – 2 7/8” x 6” J-55 tubing nipples (not used), 7/8” x 2’ UHS rod sub w/ new metalloid coating, ¾” UHS rod sample removed from Well 697 9-19-2002, 7/8” x 2’ UHS rod sub w/ metalloid coating after use in Well 697, 2 – 7/8” x 2’ UHS rod subs, ¾” UHS bare sucker rod sample.

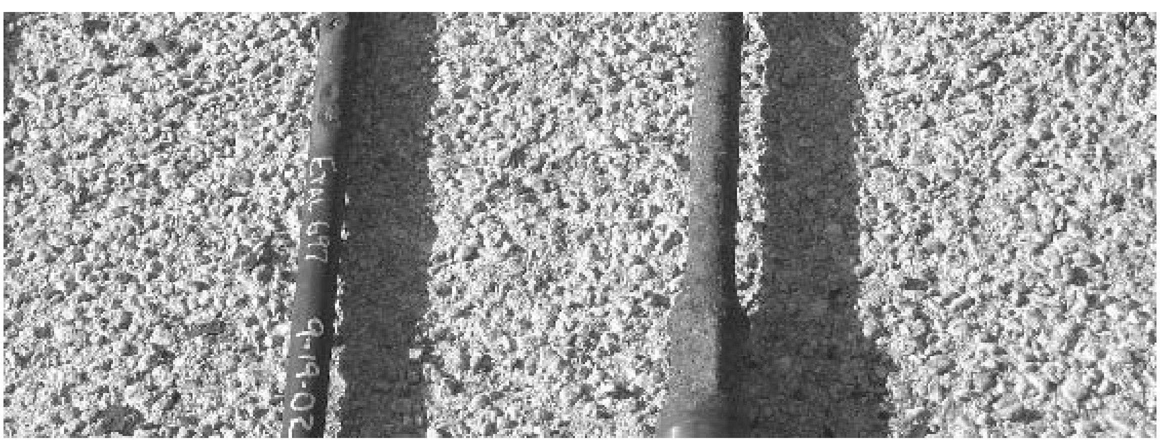


Figure 4 – Closeup view of ¾” UHS bare rod sample from Well 697 removed 9-19-2002, showing heavy pitting along a wear pattern. Also, shown is coated 7/8” UHS rod sub, with oxidized FeS scale still intact, after removal on May 6, 2004.

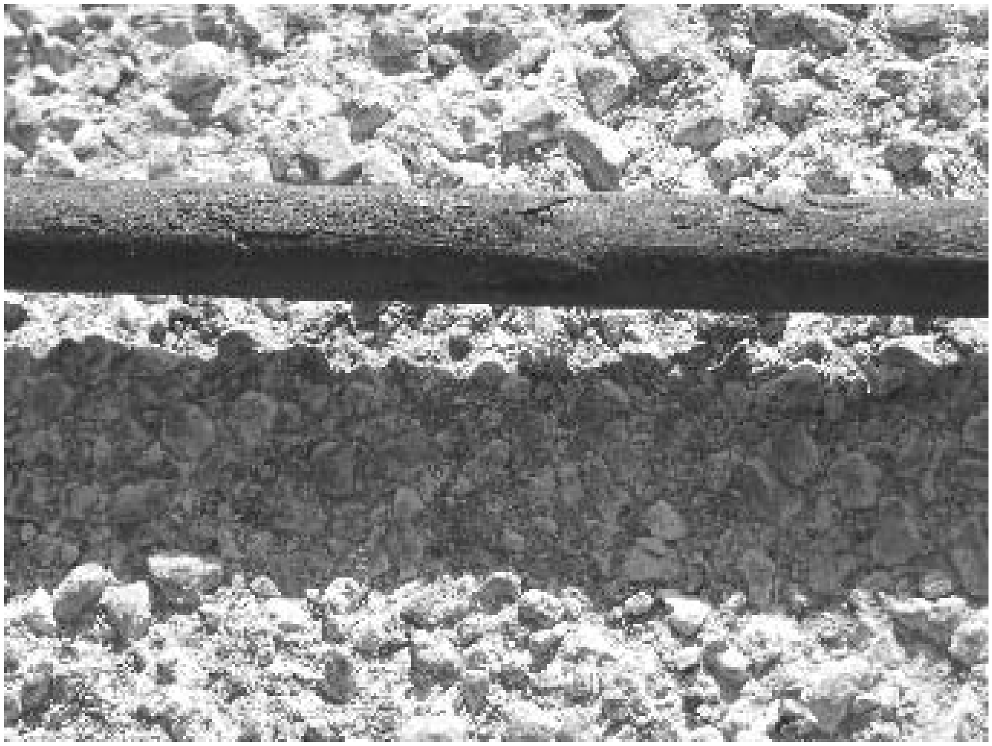


Figure 5 – Close up photo of ¾" UHS bare sucker rod sample showing spalled metal flaking from rod body, along a wear pattern. Rod sample taken from Well 697 with the coated pony rods on May 6, 2004, after being in well about 5 months.

Figure 6 – ¾" x 2 ft UHS pony rod, after being cut in half. The bottom half showing oxidized scale on it, and top half after "shot" peening. The pony rod ran for over 1 year.
The majority of the metalloid coating appears in tact.