

PROSPECTUS

A PROGRAM TO UPGRADE MATERIALS AND PROCESS STANDARDS FOR FABRICATION OF HEAVY WALL VESSELS OF 2 ¼ Cr- 1Mo- 0.25V ALLOY FOR SERVICE WITH HYDROGEN AT HIGH PRESSURES AND TEMPERATURES

***-OBJECTIVES INCLUDE ASSURANCE OF CRACK-FREE WELDS, MEETING PETROLEUM
INDUSTRY TOUGHNESS OBJECTIVES, DEVELOPING WELDING GUIDELINES,
VALIDATING HEAT TREATMENT and MPT PROCEDURES PLUS ENHANCMENT OF
SUITABILITY OF THE ALLOY FOR NEW, SIGNIFICANTLY INCREASED ELEVATED-
TEMPERATURE ALLOWABLE STRESSES-***

**- THE MPC PROJECT HPV-PREVENT WILL BE AN EXTENSION OF THE MPC INITIATIVE THAT
LED TO THE DEVELOPMENT AND COMMERCIALIZATION OF THE 2 ¼ Cr -1Mo- 0.25V ALLOY
AND RECOGNITION OF THE ALLOY BY ASME SECTION VIII DIVISION 2 and API 941**

PROGRAM BACKGROUND AND NEED

Notable events that occurred in 2008 with regard to the 2 ¼ Cr -1 Mo- 0.25V (22V) alloy are:

- 1) numerous reports of cracking of narrow-gap submerged arc welds that occurred during fabrication of heavy-wall pressure vessels and
- 2) approval of an ASME Code Case for application of the alloy at significantly increased allowable stresses to temperatures where creep and creep-fatigue must be considered

The juxtaposition of these events has led to heightened interest in and concern about the reliability and service life of heavy-wall vessels of the 22V that are already built, under construction and being planned for high-pressure, high-temperature hydrogen service. Since the alloy was introduced, but prior to 2008, hundreds of 22V vessels were built for hydrogen service with few reports of fabrication problems. Hundreds more will be built in the near future, in some cases for service at significantly higher stresses than those already completed as described below. These 22V vessels are on order at fabricators all over the world.

Despite the diversity of the sources of materials, fabricators and design issues, it is the purpose of API 934-A, -B and F to assure confidence in the integrity and safe operation of all vessels destined for the high pressure hydrogen service in refineries. These documents must disseminate the best knowledge and experience regarding 22V so that all fabricators, purchasers and refinery engineers fully understand the nature of the alloy and what is required to produce sound vessels with the desired properties. These API guidance documents are necessary because fabrication of 22V requires far greater precautions and different practices than ordinary low alloy steels. A program to address this situation by upgrading the guidance and requirements of API 934-A,-B and F is outlined below.

The cracking noted above consists of numerous, difficult to detect clusters of fine transverse cracks in the weld deposits. The cracks are intergranular and the clusters may extend nearly completely through the thickness of the narrow gap welds employed in the heavy-wall vessels. The threats of crack propagation at high temperatures due to creep, during occasional thermal cycles or on start up and shut down due to interaction with hydrogen are real and should be of concern to every vessel owner and fabricator. Where the uninitiated based fabrication practices for 22V on the fabrication “know how” used the conventional unmodified 2¼Cr-1Mo major problems have followed. To achieve the desired results during fabrication of 22V the appropriate microstructures and hardness levels in weld deposits and base metals must be obtained at every step through application of very special controls.

One source of the problem is that there sometimes appear to be significant differences between what was done during welding qualification procedures and what was done fabricating the delivered hardware, even though the same consumables were used. However, different welding parameters and thermal processing can yield noticeably different as-deposited weld hardness and toughness and, consequently, resistance to cold (hydrogen) cracking, especially for narrow gap welds in these very heavy wall vessels. Of course, other combinations of weld wire and SAW flux will further contribute to potential variability and unpredictability of weld properties and performance. We have found relevant information on this behavior in European Union reported studies and our own work.

Of concern also is that even after proper PWHT deposits made with some consumables have displayed remarkably low ductility and stress rupture lives as compared to the products developed under MPC’s activities to commercialize this alloy. Very little information has been disclosed about the high-temperature performance of welds prepared using some of the available consumables. This topic will be addressed below in connection with the greatly increased allowable stresses now permitted for this alloy under ASME rules.

Clearly the weld deposit cracking reported is a high priority issue and there are many potential causes. Some fabricators have reported finding a solution to this problem through control of the SAW flux, but specific details of the root cause of cracking have not be disclosed and are currently being treated as proprietary. However, if fitness-for-service assessments and MPT calculations are to be done correctly, the factors contributing to cracking during fabrication must be understood (i.e. root causes identified and disclosed).

It must be recognized that weld deposits of this alloy in the as-deposited condition are of considerably higher hardness than those with which some fabricators have had experience. High hardness deposits have low ductility and in many cases remarkably low toughness that renders them susceptible to easy crack initiation due to high residual stresses during fabrication. Examples of typical properties appear in the Table below. Experience has confirmed that the joint actions of residual stresses and hydrogen on hard, thick, narrow-gap shell and nozzle welds of 22V are capable of creating serious cracking problems unless the utmost care is taken. API 934-A and 934-B were intended to provide the needed guidance. These documents correctly identify many potential problems. However, more technical information needed to

find and justify solutions to specific problems that arise during fabrication. This information will enable purchasers and fabricators to specify and control the factors needed to prevent cracking and assure the desired soundness and mechanical properties of welds.

Typical Mechanical properties of a submerged-arc all-weld metal (informative)
Single wire process: 550A (AC) – 31V – 55cm/min Preheating: > 180°C Interpass: ~220°C

	Y.S.[MPa]	UTS[MPa]	Elong.[%]	Contr.[%]	ISO-V[J]	Hardness [HV10]	
As welded target values	880	1020	16.5	55	15(at RT)	295 - 325	*)
As welded unsatisfactory	1000	1200	5	5	<8	315 - 375	*)

***) High tensile strength and low ductility call for extremely careful handling of as-welded 22V components. To avoid high temperature gradients between weld zone and parent material the preheating / interpass temperatures needs to be sufficiently wider than specified and constant at least over 125 mm or the wall thickness from each side of the welding joint. Preheating / interpass temperature shall be maintained until dehydration treatment (DHT) starts.**

Industry must have better guidance to avoid the above noted problems. This is not just an issue for each company of the millions of dollars wasted by delays and repairs necessitated by the cracking encountered. Quality problems for one owner are likely to become problems for all as regulatory authorities become concerned. The owner/operator expects safety, reliability and long operating life with freedom from concern about undue risk and increased requirements for inspections (necessitated by lack of confidence in weld quality). Such expectations can only be obtained when fabrication procedures are under control and the vessels delivered possess the intended soundness and mechanical properties.

Inspection during and after fabrication may not assure the quality needed. Defects may go undetected due to limitations of equipment and inspection personnel. NDT inspection cannot verify toughness. Quality and mechanical properties are built in through control of manufacturing processes and materials. This was the intent of API 934-A and 934-B. The guidance currently provided by these documents is not yet fully adequate.

MPC and WRC have already taken steps and started a testing program to examine some of the actual consumables used in fabrication and have engaged in fact finding and investigations through overseas and domestic contacts and consultants. Some test materials and welding consumables have been secured. Several potential cracking scenarios and contributing factors have been identified. Much more must be done.

The cracking that has been observed in recent times may be the result of the interactions of many factors. It is not disputed that some fabricators may have been using “bad” batches of flux for submerged arc welding, as they have concluded and reported publicly. However, interactions of too high or too low preheating and post-heating temperatures and durations, DHT time and temperature, groove geometry, weld heat input, polarity and cooling rate, deposit chemistry, high hardness and coarse grain microstructure can lead to weld deposit cracking even with “acceptable” fluxes. Industry must move quickly to better understand the interactions of factors that may contribute to cracking and the means of mitigating adverse effects before API 934-A, -B and -F can be accepted as having fulfilled the purposes intended.

There is already a body of literature detailing difficulties some fabricators and consumable suppliers have had with achieving acceptable as-welded toughness of weld deposits for the 22V and its nearly identical sister alloy, the 2 ¼ Cr-1 Mo- .25 V-Ti-B alloy, referred to as alloy 24. It is well known that, for these vanadium containing alloys, until significant tempering is performed, the very hard, as-deposited,

unrefined weld microstructure is likely to have inadequate toughness to prevent crack cracks from initiating during fabrication. Other contributing factors are the extremely high residual stresses due to joint geometry, any thermal stresses due to heating and cooling, small weld imperfections and low levels of retained hydrogen. Researchers on European Union studies have reported that small differences in deposit composition and welding parameters can lead to very low toughness or very brittle performance during stress-rupture testing of tempered weld deposits.

Examination of API 934-A, and -B by MPC reveals many appropriate warnings. However, the documents are often light on guidance needed by the buyer to make decisions regarding the acceptability of specific practices proposed by a fabricator. For example, there are no quantitative factors to be considered as to when DHT may be used in lieu of ISR as the documents permit. The buyer is ill equipped to respond when asked to pass judgment on the amount and type of data that must be offered by the fabricator to justify and control a manufacturing procedure. Contradictory data from steel makers, fabricators and researchers must be resolved and questions about the effects of microstructure, hydrogen trapping and thermal history resolved. MPC is aware of heat treatment practices followed today that deviate from successful practices used when the alloy was first commercialized. Conversely, we are aware of fabricators that employ practices more stringent than those suggested in API 934 to assure successful results.

Some examples of where API 934-A, -B and -F require more guidance, data and information to prevent problems and implement remedial measures are as follows:

- 1) Desired weld deposit toughness requires tight control of PWHT temperature and time. The PWHT temperature limits in API 934 may not deliver the desired properties. This conclusion is reached because the time-temperature combinations proposed in API 934 are at variance with some reported tempering data in the literature and our test results. Practical and correct limits need to be established, agreed upon and followed.
- 2) There are inconsistencies and gaps in knowledge about hydrogen transport in the 22V alloy that raise questions about calculations made to support DHT and other out-gassing procedures. Some times and temperatures indicated for DHT in API's documents are not consistent with published hydrogen diffusivity values for the vanadium modified alloy. DHT guidance is critical to fabricating heavy wall vessels without cracking.
- 3) Similarly, degassing calculations to be used to determine the MPT for 22V in API934-F are questionable. Estimates of MPT made without sufficient diffusivity and solubility for hydrogen as well as long term aging and hydrogen embrittlement data for the 22V are justified today as being reasonable or conservative based on experience with unmodified 2 ¼ Cr-1 Mo or inapplicable step cooling test results. However, overly conservative can be unnecessarily costly to the owner-operator, or worse, with the benefit of data on the 22V or in hindsight following problems, conclusions drawn without data may be found to be unreasonable, non-conservative or indefensible because there was a lack of fundamental understanding of the alloy or of its hydrogen embrittlement behavior.
- 4) There are important omissions from API 934 with regard to qualifying welded construction for the higher-temperature, higher-stress applications now in ASME Section VIII Divisions 2 and 3. These stresses are nearly 30% higher than when the alloy was first introduced for ASME Code construction. Stress-rupture tests to qualify welding procedures when required involve specific stresses, specimen sizes and configurations, heat treatments, temperatures and test durations.
- 5) The toughness testing procedures for welds as specified in API 934 documents are not specific enough. The procedures should be upgraded to provide detail about preparing Charpy specimens of weld deposits to better characterize behavior in the Charpy toughness transition region. Obtaining correct estimates of toughness is essential to MPT and FFS calculations and, more important, for identifying substandard welding procedures.

Due to the above and other concerns, MPC proposes to gather and add data to upgrade and update API 934. Sponsors will obtain the necessary information to upgrade their corporate specifications if desired. This information is needed now because of the very large number of vessels being built and already in service. The possibility that materials and procedures that were used or are being implemented today are at variance with correct fabrication practices must be eliminated.

The gathering and communicating of information on 22V, so effective when MPC brought this alloy into commercial application, has not kept pace with the expansion of applications, the increased number of fabrication shops and sources of materials and the significantly (about 30%) higher allowable stresses for this alloy permitted by ASME. MPC will reactivate its highly successful joint industry heavy wall pressure vessel, "HPV", program on a subscriber basis. The objective is to PREVENT problems and eliminate the causes of substandard vessels.

SPONSORING HPV-PREVENT

The program is intended for petroleum industry producers and refiners engaged in high pressure hydrogen processing. Engineering and construction companies specifying or overseeing fabrication operations need to be involved. Fabricators, consumable suppliers and materials producers need to participate. Regulatory authorities may also join. The fee schedule will be scaled to reflect company size and the nature of the business activity as listed below. The completion of the total Program is estimated to require 2-3 years, with high priority tasks completed first. Subscription payments may be made in up to three installments under terms of MPC's Agreement with sponsors. The total project budget is estimated to exceed \$1.5 million dollars.

- Large Refiner Owners
- Medium Refiner Owners
- Small Refiner Owners
- Large Engineering and Construction Companies
- Engineering Consulting Companies
- Large Fabricators
- Medium Fabricators
- Material Producers
- Welding Consumable Suppliers
- Other Interested parties

Further Details are available from 22Vusersgroup@forengineers.org and mprager@forengineers.org

Please use the Reply form to indicate your organization's interest in participating.

An initial meeting for prospective sponsor's only will be held in January 2009

THE PROGRAM

The program is divided into a variety of Tasks. Some Tasks should be organized to interact while others need to be expedited due to their urgently needed input for manufacturing vessels already in production or about to be started. These Tasks will obtain evidence of the relationships among chemical composition, welding procedures, heat treatment (DHT/ISR/PWHT) needed to assure desired microstructure, hardness, toughness, quality and long term performance.

TASK 1 – SOLUTIONS TO TRANSVERSE WELD CRACKING PROBLEMS

TASK 2 – IDENTIFICATION OF ACCEPTABLE WELDING PARAMETERS

TASK 3 – MINIMIZATION OF RESIDUAL STRESSES ASSOCIATED WITH THICK, NARROW GAP WELDS

TASK 4 – IMPROVING TOUGHNESS RESPONSE OF WELDS TO HEAT TREATMENT

TASK 5 – MICROSTRUCTURAL CHARACTERIZATION OF UNSATISFACTORY WELD DEPOSITS

TASK 6 – QUANTIFYING HYDROGEN DIFFUSION AND TRAPPING BEHAVIOR FOR IMPROVED DHT AND DEGASSING PROCEDURES AND PREDICTION

TASK 7 – IMPROVED ESTIMATE OF EFFECTS OF LONG TERM SERVICE ON TOUGHNESS AND DEVELOPMENT OF CORRECT STEP COOLING PROCEDURES

TASK 8 – UNDERSTANDING AND CALCULATING EFFECTS OF INTERNAL AND EXTERNAL HYDROGEN ON TOUGHNESS OF BASE METAL AND WELD DEPOSITS FOR FFS AND MPT CALCULATIONS

TASK 9 – DETERMINING THE EFFECTS OF STRAIN CYCLING ON LOCAL CREEP DAMAGE AT VESSEL STRUCTURAL DISCONTINUITIES

TASK 10 – VALIDATION OF SUITABILITY OF WELDING PROCEDURES FOR SERVICE UP TO THE CREEP RANGE AS DEFINED IN ASME RULES

TASK 11 – ADVANCED CONCEPTS IN HYDROGEN ATTACK

TASK 12 – REPAIR GUIDELINES

TASK 13 – DISSIMILAR METAL WELDING

TASK 14 – QUALITY ASSURANCE ISSUES

TASK 15 – MPT GUIDELINES

TASK SUMMARIES

Comprehensive Task details will be provided to those indicating serious intent to sign the agreement to sponsor the program. Task scopes and approaches may be modified in accord with the preferences of sponsors. There is no desire to duplicate work that has been done, for example under European Union sponsorship. The program is intended to build on the foundations of such work to better understand, validate and extend the conclusions.

TASK 1 – SOLUTIONS TO TRANSVERSE WELD CRACKING PROBLEMS

The objective of this Task is to determine how composition and microstructure lead to crack initiation. It will contribute to understanding how control of welding variables such as heat input, cooling rate, bead size and deposit hardness can be controlled to reduce cracking susceptibility. Consideration will be given to the CCT diagram and the role of carbon content, transformation temperatures and products as well as the nature of phases formed during solidification and the effects of impurities. Samples of actual welds will be used for microstructural evaluations and mechanical property testing. It has been suggested that the effects of a “bad flux” can be demonstrated using a test to determine the short-time, elevated

temperature ductility of a weld deposit made with the flux. It has been suggested that if this concept appears to have merit an “international” round robin might be conducted under this Task under this task to establish a standard test procedure and specimen. Commercial fluxes and wires will be used. Limits on impurities will be identified in this Task.

TASK 2 – IDENTIFICATION OF ACCEPTABLE WELDING PARAMETERS

Narrow gap welds will be made and subjected to PWHT to establish the welding parameters with which satisfactory toughness and other mechanical properties can be achieved. The objective will be to establish ranges for welding parameters and exclude detrimental factors such as excessive heat input and bead size. Procedure specifications will be written to enable processes to be effectively monitored. Variables include preheat, polarity, heat input, wire size, bead overlap etc.

TASK 3 – MINIMIZATION OF RESIDUAL STRESSES ASSOCIATED WITH THICK, NARROW GAP WELDS

This Task will interact with PVRC’s Phase II project with Battelle’s Dr. Pingsha Dong to develop and validate procedures for residual stress prediction. PVRC has already identified narrow gap welds as a high priority concern. With support from the HPV-PREVENT project the matrix of welding parameters, joint geometries, heat inputs and material properties can be expanded.

TASK 4 – IMPROVING AND UNDERSTANDING TOUGHNESS RESPONSE OF WELDS TO HEAT TREATMENT

This Task will interact with Task 2 and explore the effects of reheating cycles and heat input on toughness behavior as a function of ISR and PWHT time and temperature. Attention will be paid to the effect of microstructure where the notch is placed in CVN specimens. The objective is to provide more useful estimates of toughness for quality assurance, FFS assessment and MPT calculations. Minimum PWHT temperatures and times will be determined to assure the desired toughness in the weld deposit.

TASK 5 – MICROSTRUCTURAL CHARACTERIZATION OF UNSATISFACTORY WELD DEPOSITS

In concert with Task 4 toughness test results will be gathered from welds made for this project and from other sources to create an atlas of microstructures in order that small specimen sampling or replication can be used to evaluate welds in vessels in the field or upon completion of fabrication. Comparison of the delivered microstructures and hardness values in vessels with characterized samples will enable better estimates of properties to be made.

TASK 6 – QUANTIFYING HYDROGEN DIFFUSION AND TRAPPING BEHAVIOR FOR IMPROVED DHT AND DEGASSING PROCEDURES AND PREDICTION

This Task will use thermal rather than electrochemical methods of charging hydrogen to study diffusion and hydrogen trapping. The effect of microstructure on diffusivity will be studied using welded deposits and base metal with microstructural conditions representative of those achieved during DHT, ISR and PWHT. Minimum DHT temperatures and times will be validated for specific geometries using FEA and sample tests for the observed trapping conditions.

TASK 7 – IMPROVED ESTIMATE OF EFFECTS OF LONG TERM SERVICE ON TOUGHNESS AND DEVELOPMENT OF CORRECT STEP COOLING PROCEDURES

The emphasis will be on weld deposits which may have higher levels of impurities in order to establish compositional limits to minimize in service embrittlement. An effective step cooling procedure for 22V will be established to replace procedures adopted from other alloys.

TASK 8 – UNDERSTANDING AND CALCULATING EFFECTS OF INTERNAL AND EXTERNAL HYDROGEN ON TOUGHNESS OF BASE METAL AND WELD DEPOSITS FOR FFS AND MPT CALCULATIONS

This Task will use thermally charged and environmentally exposed specimens to obtain the most relevant data on toughness impairment by hydrogen. The matrix will include materials of differing tensile and initial toughness properties. This task may result in relaxation of stringent MPT and FFS procedures developed based on the same assumptions used for conventional 2 ¼ Cr-1 Mo steel.

TASK 9 – DETERMINING THE EFFECTS OF STRAIN CYCLING ON LOCAL CREEP DAMAGE AT VESSEL STRUCTURAL DISCONTINUITIES

The new model for the interaction of creep and strain cycling approved for 22V applications under ASME can be improved with additional long hold time cyclic data to remove excess conservatism. A matrix has been developed and proposed to ASME. There are many potential applications of this new model where high-strength, low alloy steels are used at high temperatures. These applications include turbine rotors used in refineries and other elevated temperature electric power applications as well as advanced nuclear plants being developed under international cooperative studies. The potential for a cooperative research program exists.

TASK 10 – VALIDATING SUITABILITY OF WELDING PROCEDURES FOR SERVICE UP TO THE CREEP RANGE AS DEFINED IN ASME RULES

This TASK will fill in missing data on the stress-rupture behavior of 22V weldments. Welded, high-strength Cr-Mo-V steels display severe life reductions as compared to base metal due to degraded creep resistance in the fine grain regions of heat affected zones. This degradation leads to failures classified as Type IV which currently plague the electric power industry where advanced Cr-Mo-V steels have been applied. Type IV failures may occur in the HAZ regions within narrow gap weld deposits as well as in the HAZ of the adjacent base metal. ASME requirements include testing to demonstrate that 22V welds perform substantially as well as base metal. This requirement has been overlooked in 934-A and -B. This Task will interact with Tasks 3 and 9 because improved characterization of creep properties of 22V base metal, HAZ and weld deposits is necessary for calculations in these tasks. To estimate cyclic life in the creep range under the new ASME Code Case creep damage must be calculated using FEA modeling to identify the most severe “multiaxial stress hot spots”. Then welds are located, away from the hot spots, to regions where their reduced HAZ strengths are adequate.

TASK 11 – ADVANCED CONCEPTS IN HYDROGEN ATTACK

The original investigation aimed at including 22V in API 941 was only an exploratory investigation consisting of only a few tests and did not envision the higher allowable stresses now permitted in high pressure hydrogen service . This Task will incorporate tests planned utilizing the new understanding of HTHA developed for the API 941 Technical Basis document and explore concerns about the effects of multiaxial loads at stress concentrations.

TASK 12 – REPAIR GUIDELINES

This Task will develop guidelines for controlled deposition welding, minimizing residual stresses local preheating, post heating, DHT and local PWHT. The appropriateness of under-matching consumables will be considered. There needs to be an understanding of the special precautions required when repair welding vessels of this hydrogen trapping material.

TASK 13 – DISSIMILAR METAL WELDING

This Task will establish special guidelines for joining very high strength Cr-Mo-V alloy steels to high expansion low strength, austenitic alloys and with regard to weld overlays. The potential for

carburization and decarburization during PWHT and in service aging at elevated temperatures will be explored. Preferred joint preparations and consumable selection will be reported.

TASK 14 – QUALITY ASSURANCE ISSUES

This activity will identify and specify any special compositional limits to be placed on fluxes and on wires, flux drying procedures, base metal and weld deposit compositional factors necessary to minimize long term embrittlement, hardness limits, TOFD and Phased array procedures for narrow gap welds etc.. It is important to relate specific residual stress material conditions and potential cracking mode at each step of the manufacturing procedures to the inspection methods to be used with due consideration of the toughness level and cracking mode possible at that stage of processing.

TASK 15 – MPT GUIDELINES

MPT Guidelines for 934-F will be written so that they interface well with the API/ASME FFS concepts and the specific characteristics of 22V alloy. They are now derivative of the procedures used for the conventional low chromium steels and may be overly conservative.



MARTIN PRAGER
EXECUTIVE DIRECTOR

SPONSORSHIP REPLY FORM

A PROGRAM TO UPGRADE MATERIALS AND PROCESS STANDARDS FOR FABRICATION OF HEAVY WALL VESSELS OF 2 ¼ Cr- 1Mo- 0.25V ALLOY FOR SERVICE WITH HYDROGEN AT HIGH PRESSURES AND TEMPERATURES

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INCREASED ELEVATED-TEMPERATURE ALLOWABLE STRESSES-*

Reply to: 22Vusersgroup@forengineers.org Industry Sector _____

COMPANY _____

CONTACT INDIVIDUAL'S NAME _____

CONTACT'S E-Mail _____

CONTACT MAILING ADDRESS _____

TELEPHONE _____

- My organization is interested in sponsoring the identified program and wishes to send a representative to the launch meeting in January- please send further details and budgeting information for our size and type of organization
- My organization is interested in sponsoring the identified program but cannot send a representative to the launch meeting in January- please send further details and budgeting information for our size and type of organization
- My organization is not interested in sponsoring the identified program
- MPC--Please see the attached for comments on the program plan**