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Integrated Modeling and Characterization of Local Crack Chemistry

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Integrated Modeling and Characterization of Local Crack Chemistry

Abstract

The MULTEQ computer program has become an industry wide tool which can be used to calculate the chemical composition in a flow occluded region as the solution within concentrates due to a local boiling process. These results can be used to assess corrosion concerns in plant equipment such as steam generators. Corrosion modeling attempts to quantify corrosion assessments by accounting for the mass transport processes involved in the corrosion mechanism. MULTEQ has played an ever increasing role in defining the local chemistry for such corrosion models. This paper will outline how the integration of corrosion modeling with the analysis of corrosion films and deposits can lead to the development of a useful modeling tool, wherein MULTEQ is interactively linked to a diffusion and migration transport process. This would provide a capability to make detailed inferences of the local crack chemistry based on the analyses of the local corrosion films and deposits inside a crack and thus provide guidance for chemical fixes to avoid cracking. This methodology is demonstrated for a simple example of a cracked tube. This application points out the utility of coupling MULTEQ with a mass transport process and the feasibility of an option in a future version of MULTEQ that would permit relating film and deposit analyses to the local chemical environment. This would increase the amount of information obtained from removed tube analyses and laboratory testing that can contribute to an overall program for mitigating tubing and crevice corrosion.

INTRODUCTION

Corrosion of heat transfer tubing in nuclear steam generators has been reported by EPRI as a persistent problem in the power generation industry. Intergranular attack (IGA) and intergranular stress corrosion cracking (IGSCC) continues to be a major cause of tube degradation and steam generator replacement for Alloy 600 tubed units. The attack appears to occur in regions of chemical concentration: sludge pile crevices and tube support plate crevices. Small amounts of chemical species in the bulk water can have significant effects on the local chemistry of a concentrating crevice. The MULTEQ computer program has become an industry wide tool which can be used to calculate the chemical composition of a solution in a crevice or flow occluded region as the solution concentrates due to local boiling. These results can be used to infer the local chemistry at a potential corrosion site and thereby assess corrosion susceptibility as a function of the bulk chemistry measured in the plant.

Corrosion models quantify the relationship between the bulk environment and the local corrosion rate. In so doing, these models can be used to optimally schedule downtime for inspections and cleanings and assess the viability of possible fixes, such as inhibitors to preclude the need for steam generator replacements. The corrosion models are capable of determining rates because the necessary mass transport processes for the corrosion phenomenon have been built into the models. For an integrated corrosion model, the transport processes must ultimately determine the mass exchange rate between the bulk water environment and the local corrosion site. In doing so, numerous computer codes are employed to make the necessary linkage between the bulk environment and the local corrosion site. Thermal and hydraulic steam generator codes, such as ATHOS3, can make the link between the bulk chemical concentration and the "near local" chemical concentration near a flow occlusion in a plant while general purpose codes, such as FLOW3D, can make the link to the local chemical concentration within the flow occlusion. The link from this point to the metal surface then can be made through specialized models, which are the topic of this paper, that account for the microscopic mass transport phenomena that occur between the dissolving metal surface and the concentrated local chemistry. MULTEQ plays an important role in each regime in determining the speciation of the chemistry at each step in the concentration process.

Integrated Modeling Approach

An integrated modeling approach to IGA/SCC of Alloy 600 will need to focus the efforts of diverse groups of specialists allocated to manage the corrosion problem. This approach is centered around a corrosion model, which relates the metal dissolution process at the corrosion site (the corrosion rate)

to observables such as bulk chemistry, trace elements, and hideout data (Figure (1)). During the course of managing the corrosion problem, the model undergoes continuous development as plant and laboratory data are compared against model predictions.

The model should integrate information from the wide range of laboratory and plant data that is acquired during the course of managing the corrosion problem. This can assist in the interpretation of experimental results with a minimum of bias. In linking the local corrosion mechanism to measurable bulk parameters, the model also aids in the design of more prototypic tests, by showing how bulk parameters need to be controlled in order to accurately simulate a corrosion environment occurring in a plant. Since the model provides a focus for laboratory testing and analysis, it is crucial that an integrated model be put forth early in the program

In the best of worlds, the integrated model develops, incrementally and without significant changes to the basic premises of the model, to encompass an increasingly wider range of conditions and to provide a more detailed picture of the corrosion process. However, a positive approach should still be taken when radical changes to the basic premises of the model are necessary to achieve consistency with new or more accurate data. This is often an indication of significant progress in understanding the corrosion process.

This paper will outline how the integration of corrosion modeling with the analysis of corrosion films and deposits can lead to the development of a useful modeling tool, wherein MULTEQ is interactively linked to a diffusion migration transport process. This tool can provide the capability to make detailed inferences of the local chemistry based on the analyses of the local films and deposits inside a crack. In so doing, the comparison of film and deposit analyses of plant and laboratory specimens, can be used to better check that the laboratory tests are an accurate simulation of the plant and to provide additional information on the transport processes that can contribute to more reliable corrosion model predictions with which to base decisions necessary for reliable plant equipment operations.

Corrosion Films and Deposits

Corrosion films and deposits form under nonequilibrium conditions in the presence of chemical gradients caused by the metal dissolution process. The corrosion film grows into the base metal by a solid state mechanism involving the migration of vacancies and interstitial defects through the film, Figure (2). The corrosion deposit forms from the precipitation of chemical species out of solution near the film. The chemical environment at the film/solution interface plays an important role in controlling both the rate of the metal dissolution, film growth, and precipitation processes. These processes, in turn, establish chemical gradients in the neighboring solution and thereby change the local chemical environment. In so doing, at this microscopic level, the chemical environment and the corrosion process are strongly coupled. The composition of films and deposits are a reflection of the local environment from which they formed and gradients in the composition can signify the presence of a chemical solution gradient at the time of formation.

The full extent to which the composition of corrosion films and deposits can be used to characterize the local chemical environment remains to be demonstrated. This is dependent on the spatial detail with which the deposits and films can be analyzed and on the modeling tools which are needed to interpret the results.

Analysis with AEM and Raman Spectroscopy

Cross sectional AEM and Raman are two analytical techniques that can provide the needed characterization of corrosion films and deposits. The results of these techniques can be used empirically to compare corrosion films and deposits produced in laboratory specimens with those found on field components. These analyses provide important checks to insure that the laboratory test environment is representative of the plant component environment.

AEM can be used to image internal microstructures and qualitatively assess the porosity and permeability of corrosion films and deposits inside cracks. It can also provide a semiquantitative analysis of the elements and determine compound information from the crystal structure. A key application of AEM is to obtain an analysis of the crack face and tip in profile. Although AEM is an extremely powerful tool, specimen preparation can be difficult since the samples must be electron transparent.

Raman can complement AEM analysis and provide additional compound information of the corrosion films and deposits in a crack. Raman spectra of isolated crystals within the deposit or film can be compared against known compounds in a Raman library. This method can be used to probe the chemical compounds in the deposits and films on the surface of an open crack face.

Corrosion Films on Alloy 600

Cross sectional AEM has been used to determine the composition of the films and deposits along cracks in Alloy 600 which was exposed to the following bulk chemical environments; caustic, acid sulfate and AVT with oxidizing sludge. This data was previously introduced by Bussert et al.¹

In the caustic environment, cracks propagated down grain boundaries with and without carbides. When carbides were present, they were preferentially attacked and showed evidence of NiCr_2O_4 (Figure (3)).

In the acid sulfate environment, cracking occurred along the chromium depletion layer near the grain boundary. The oxide layer was reported as complex and porous, possibly containing NiCr_2O_4 and Ni_xS_y (Figure (4)).

In the environment consisting of AVT with oxidizing sludge, cracking occurred along the chromium depletion layer near the grain boundary. The corrosion product was primarily NiO (Figure (5)).

The nickel and chromium content of the corrosion films on Alloy 600 has been used to infer the local pH of the environment². Exposure at temperature to acidic, neutral, and mildly alkaline chemistry produces a chromium-enriched oxide layer on Alloy 600 while exposure to more caustic environments tends to produce a nickel enriched oxide layer. The plot in Figure (6) was produced from data by Sakai et al.³, based on Auger electron spectroscopy analysis Alloy 600 specimens exposed to different pH environments at high temperature. This effect appears to be based on the different thermodynamic stabilities of the metal oxides of Alloy 600 as a function of the pH.

The researchers, in Reference (1), prescribed a methodology for investigating the crack chemistry based on the observed films (Figures (7)). This methodology consisted of a detailed multidisciplinary analysis of the crack deposits and chemistry through such tools as AEM and Raman for deposit and film analysis, in-situ Raman to study the chemistry in the crack, and electrochemical tests to map the bulk chemistry as a function of the electrochemical potential. MULTEQ can play an important role in such an integrated approach to study a corrosion process. With respect to a crack interior environment, MULTEQ, coupled with a diffusion and migration mass transport model, could be used to interpret this detailed information.

Application: MULTEQ Coupled with a Transport Model

MULTEQ is a computer program which calculates the equilibrium composition and pH of an aqueous solution. In Figure (8) are shown the results of a series of MULTEQ calculations for the ratio of nickel to chromium in the thermodynamically stable oxides of Alloy 600 with respect to pH for three values of elemental nickel, chromium, and iron, that were input to MULTEQ in proportions equal to that of Alloy 600. (These calculations require a database that includes the solubilities of the typical oxides found on Alloy 600; NiO , NiFe_2O_4 , NiCr_2O_4 and Cr_2O_3 ^{4,5}.) The compositions of the thermodynamically stable oxides are sensitive to pH, however the three curves each show a decrease in the nickel to

chromium ratio of the oxides at high pH which is opposite to the trend observed from elemental analyses of real films formed on Alloy 600. This decrease in the nickel to chromium ratio in the stable oxides results from the increased stability of nickel metal at higher pH. An actual film on Alloy 600, exposed to a high pH solution, could be a mixture of metal oxides and precipitated nickel metal. In order to relate the observed results to the calculated result, one would need to know how the elemental nickel is distributed throughout the combined alloy and film system of the calculation. This cannot be done by an equilibrium code, such as MULTEQ, since distribution of elemental nickel would depend on the rates of mass transport processes taking place near the metal surface during film formation. Additionally, these MULTEQ results show that the calculated ratio of nickel to chromium in the oxide is a function of the amounts of elemental nickel, chromium, and iron initially input to the calculation. Again, the amount of alloy needed to match an observed Ni/Cr ratio would depend the rates of mass transport processes taking place during film formation.

The basic mass transport processes involved in the formation of corrosion films and deposits need to be taken into account in order to use film and deposit analyses to reliably extract information on the local chemical environment. One approach might be to link MULTEQ to a simple diffusion and migration transport model in order to better represent the change in chemistry near the metal surface. The boundary conditions for such a model would be specified by the species concentrations at some distance away from the surface, along with the metal dissolution rate. This modeling tool could be used to provide a more detailed inference of the local chemical environment at the corrosion site as a function of the film and deposit composition as revealed by such techniques as AEM and Raman.

Application to a Crack Deposit

To demonstrate the value of an integrated approach between modeling, microanalysis, laboratory testing groups, available data from a cracked tube was reviewed from Reference (1). The tube was 300 series stainless steel from a test loop boiler which had been subjected to abnormal stress. The crack occurred in under deposit regions. When removed, the crack was found to be packed with deposits.

Characterization of Films and Deposits (AEM and Raman)

Preliminary data showed that the crack deposits contained a mixture of metal oxides (spinel), some nickel sulfides, and metal hydroxyphosphates. These deposits appeared to be porous and permeable. At the metal/film interface, there was a coherent layer of nonporous mixed metal spinel. Secondary side chemical species, present in the boiler water, were not found at the metal/film interface. This is depicted in Figure (9).

As might often is the case, the analyses of the deposits, did not discern a consistent trend in the chemical composition of the deposit with distance into the crack. From such data, it could be assumed that the chemistry inside the crack was relatively uniform. Use of MULTEQ was attempted to illustrate that such an assumption may not be proper for a tube crack which might be expected to show a chemical gradient (Figure(10)). Elemental iron, nickel, and chromium, in proportions representative of stainless steel, were included in the input to a MULTEQ setup along with the specifications for a concentrated bulk chemistry¹. The amount of elemental metal included in the input was chosen to match the type of precipitates observed by the deposit analysis to date. The precipitates that were predicted to form were in general agreement with the deposit analysis. However, the crystal structures of specific metal phosphates, sodium iron phosphate and sodium iron hydroxyphosphate, had not been accounted for (Figure(11)). Such findings suggest clear variations in the chemical composition of the crack deposit. For example, sodium iron hydroxyphosphate was more prevalent near the crack mouth region while sodium iron phosphate was more prevalent at the crack tip region.

¹ Some metal hydroxyphosphate compounds were included to reflect the deposit findings.

MULTEQ was incapable of reproducing these results due to the assumed uniform crack chemistry. Such an inconsistency between the deposit analysis and the calculations is likely a typical case and leads to the consideration that a chemical gradient exists within a crack of this nature.

Interactive Coupling of MULTEQ with a Diffusion and Migration Transport Model

According to steady state one dimensional diffusion and migration transport models, a flux of ions from a surface will establish a chemical gradient in a solution by accelerating the transport of anions and hindering the transport of cations to the surface, Figure(12). For crack in Alloy 600, a flux of nickel or chromium ions from the dissolving crack tip would likely establish a chemical gradient within the crack.

MULTEQ can be interactively coupled to a one dimensional steady state diffusion migration model that allows for a flux of metal ions from the crack tip (as a result of metal dissolution) to produce a chemical gradient in the crack, Figure(13). This flux can be specified as a function of the measured crack rate. This coupling can be made through a UNIX shell in which MULTEQ functions as a stand alone program that interfaces with the diffusion and migration model. In this way, the standard output from MULTEQ provides input to the transport model, which in turn, produces input for the next MULTEQ run. The calculation starts at the crack mouth and proceeds incrementally toward the crack tip. In general, an equilibrium code, such as MULTEQ, can be coupled to a steady state mass transport process, if the chemical reactions in the code are assumed to be infinitely fast and reversible or infinitely slow and irreversible. These two special cases, require no additional rate data and will be referred to as Option 1 reactions and Option 2 reactions, respectively. Option 1 reactions directly couple and feedback to the mass transport model. These reactions will affect the local chemistry. An Option 2 reaction, being infinitely slow and reversible, will only require a passive coupling to the transport model.

For example, the deposit morphology in the stainless steel case agreed with the film and deposit analysis (Figure (14)) when reactions for the metal phosphate precipitates were assumed to be Option 2 and all other reactions were assumed to be Option 1. This shows promise for reconciling similar observations in Alloy 600 cracks with varied deposit formations in three cracking environments reported in Reference (4).

Implications for Alloy 600 SCC

A detailed picture can emerge about the local chemistry in a crack, based on a comparison of the crack film and deposit analysis with predictions from a tool which embodies capabilities to deal with high temperature complex chemical equilibria and mass transport through a diffusion and migration mechanism (Figure (15)).

- pH can change with distance into the crack
- deposit formation may or may not influence the local crack chemistry
- specific chemical conditions might be identified by the presence of specific compounds.

This method is recommended to survey local crack chemistries for Alloy 600 IGA/SCC. The metal ion flux, calculated from a measured crack rate, could be input to the model. By specifying a concentrated faulted water chemistry for the crack mouth, MULTEQ, coupled with the simple diffusion migration model, could be used to evaluate the local chemistry, and the deposit and film composition within a crack.

One of the driving forces behind this approach is to highlight a method to build upon existing technology (i.e., MULTEQ) in developing new tools with which to better assess corrosion processes in steam generators. In the approach presented in this paper, the MULTEQ computer program was purposely not altered, when coupled to the transport process. This points out the feasibility, perhaps someday, of an option in a future version of MULTEQ, that could better relate film and deposit analyses to the local chemical environment.

Potential Application for Assessing Inhibitors for IGA and SCC

A model, such as the one described in the current paper, could use the above results to begin to infer the pH profile in a crack as a function of the bulk chemical environment. As an example, one could use a flux of nickel or chromium to model the crack chemistry in a caustic crack with carbides. This might provide a detailed characterization of the local crack chemistry, which could prove valuable in assessing potential fixes such as inhibitors for IGA/SCC.

The EPRI Secondary Side IGA/SCC Inhibitor Program has considered the use of titanium oxide based compounds as potential inhibitors for IGA/SCC. The inhibiting effect has been attributed to the formation of a more protective film on Alloy 600 that incorporates titanium, possibly in the form of nickel titanate. Since the solubility of titanium dioxide increases with increasing pH⁸, conditions that reduce the pH in the crack, might decrease the effectiveness of this inhibitor. A model, like the one described in this paper, could be used to assess the conditions under which titanium in the bulk chemistry could reach the crack interior in sufficient concentration to form nickel titanate (Figure(16)).

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Figure 1

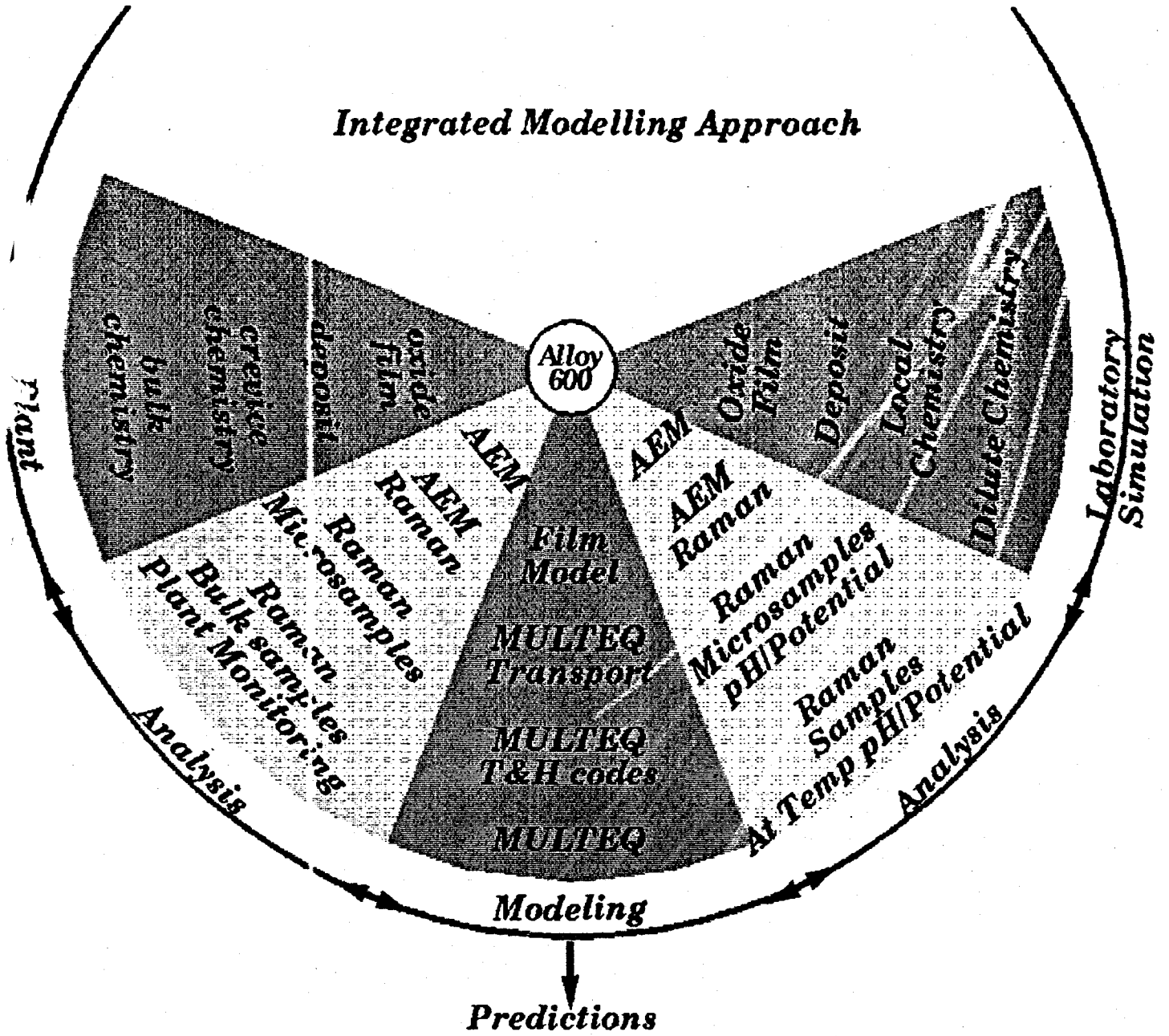


Figure (2)

Corrosion Films and Deposits

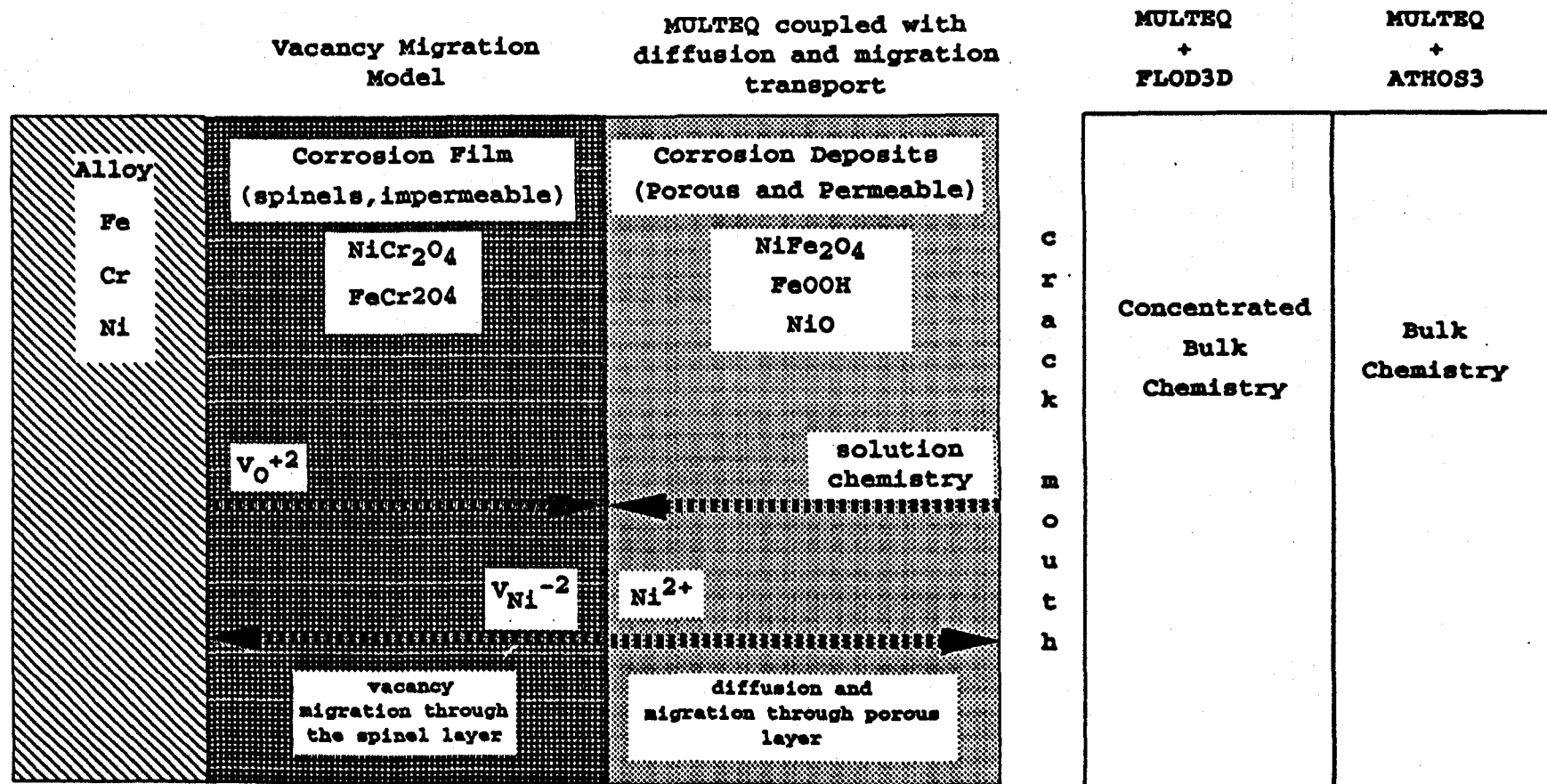


Figure (3)

SUMMARY OF FINDINGS CAUSTIC EXPOSED SPECIMEN

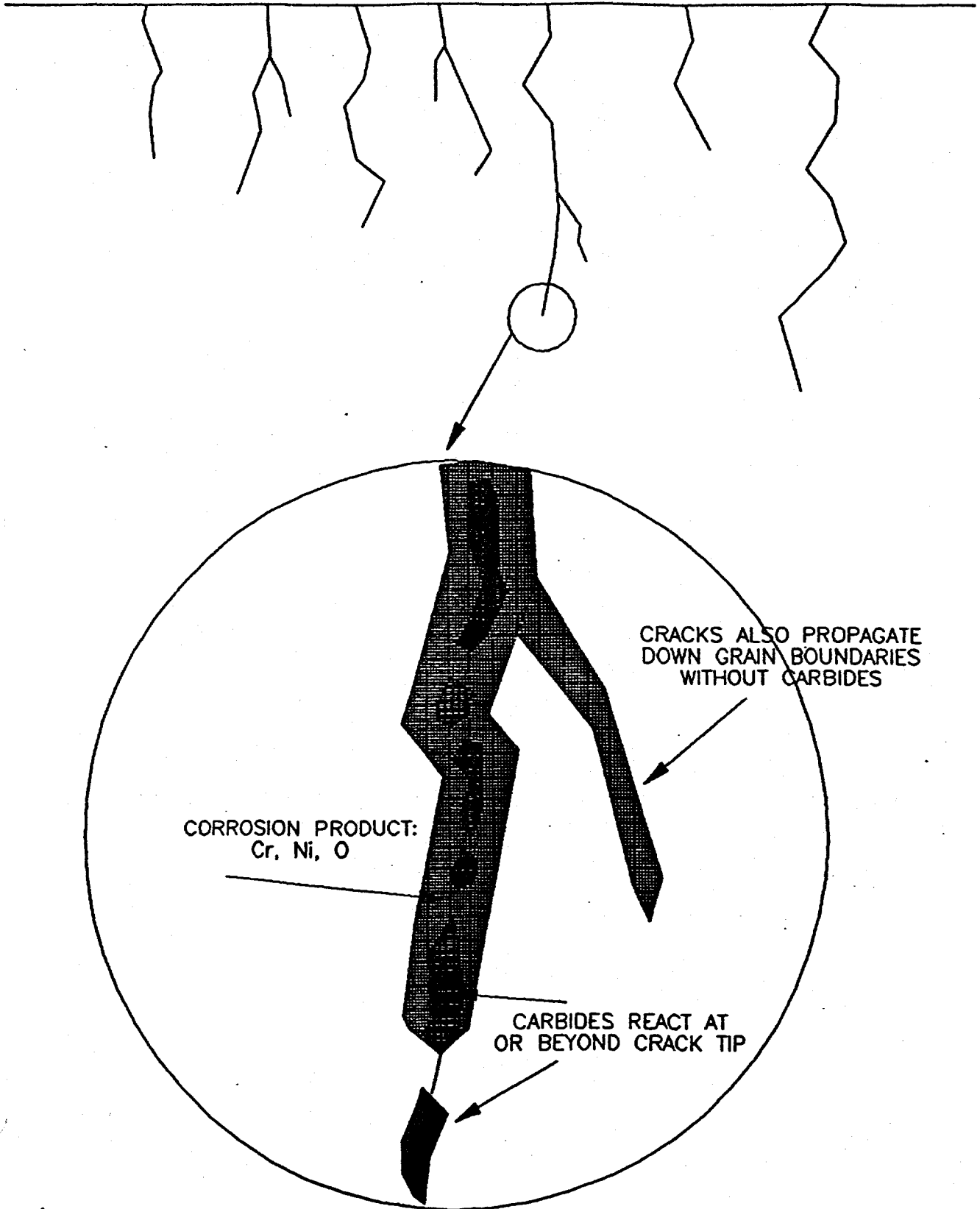


Figure (4)

SUMMARY OF FINDINGS ACID SULFATE EXPOSED SPECIMEN

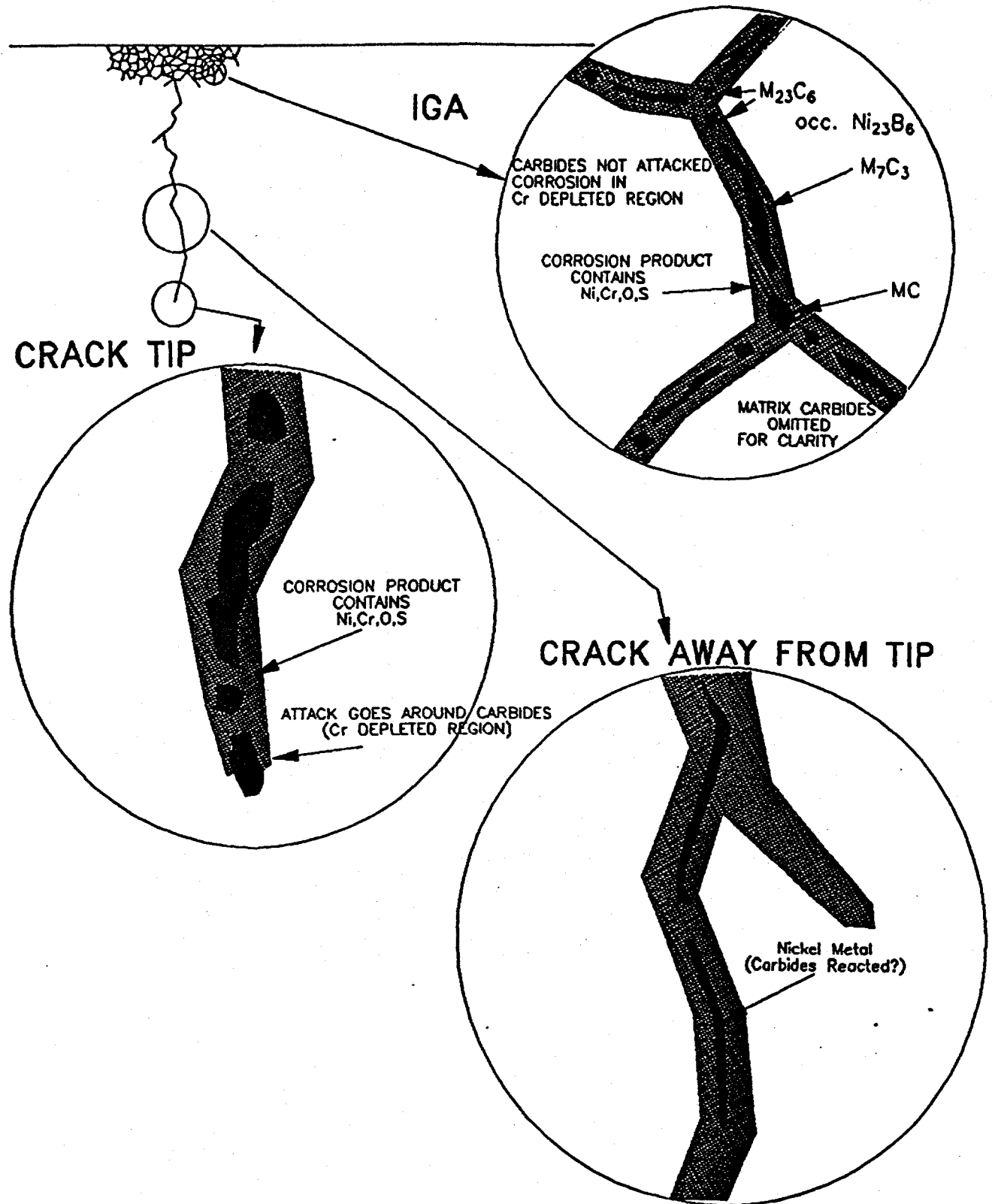


Figure (5)

SUMMARY OF FINDINGS:
EXPOSURE TO AVT CHEMISTRY
WITH OXIDIZING SLUDGE

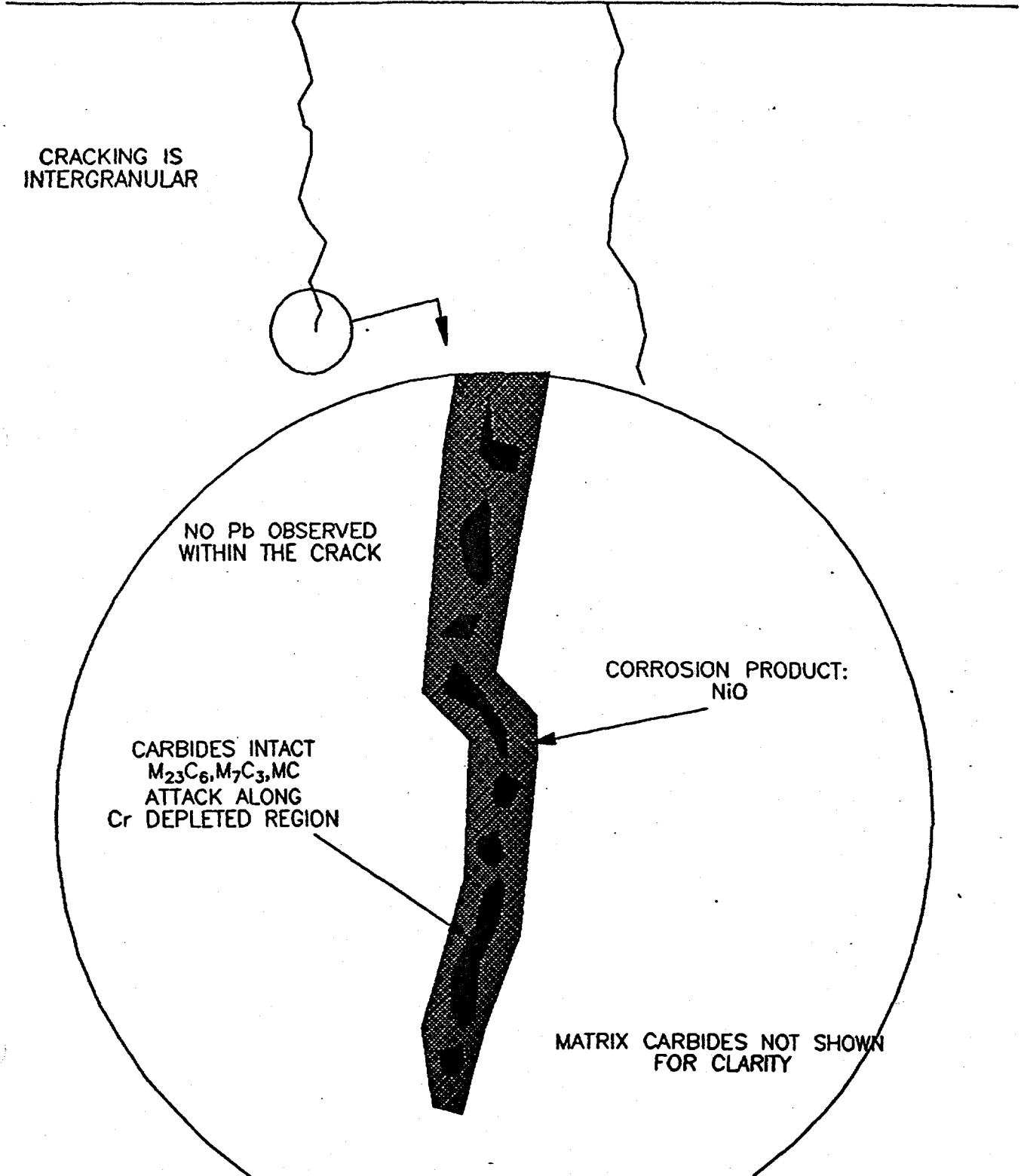


Figure (6)

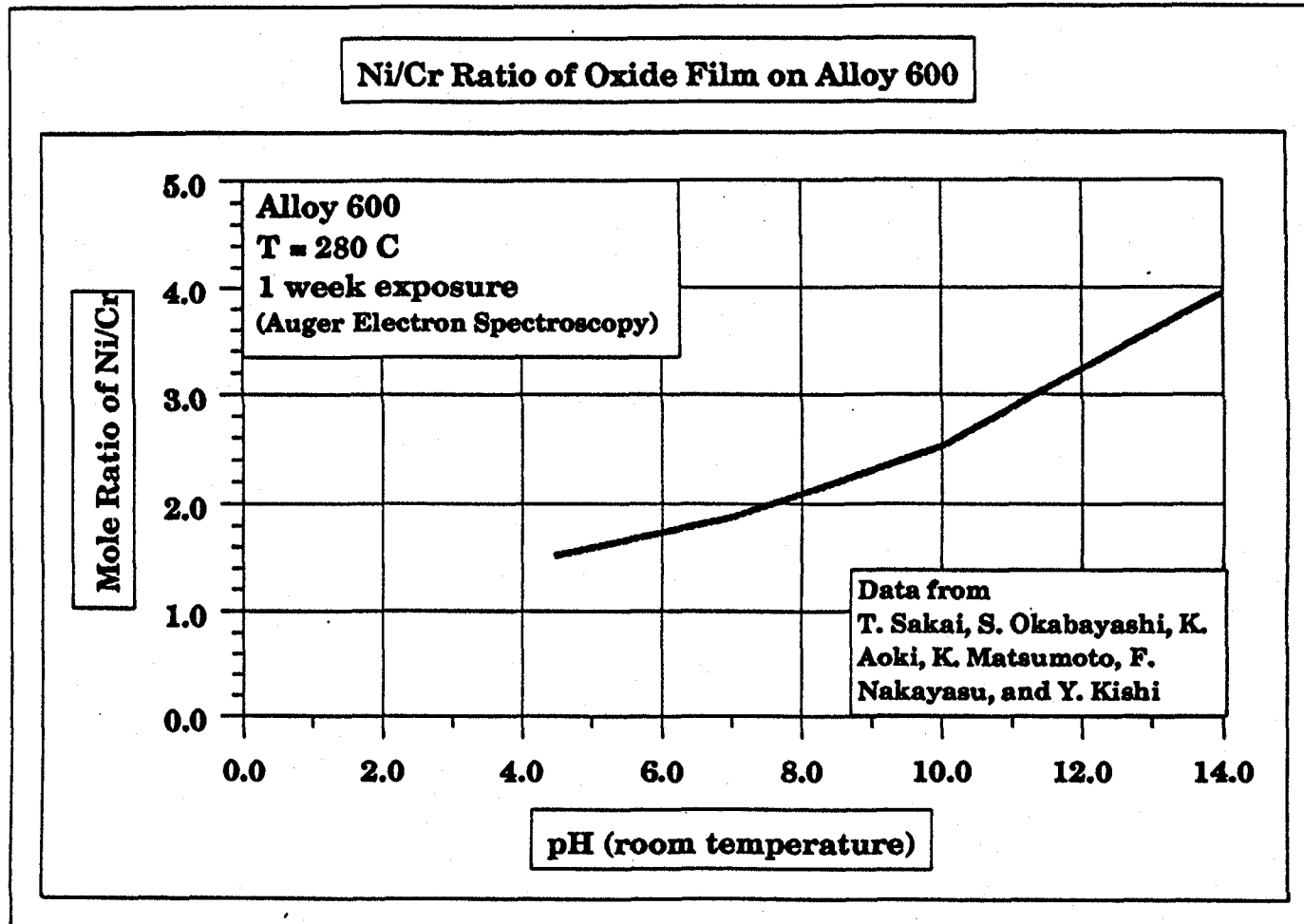
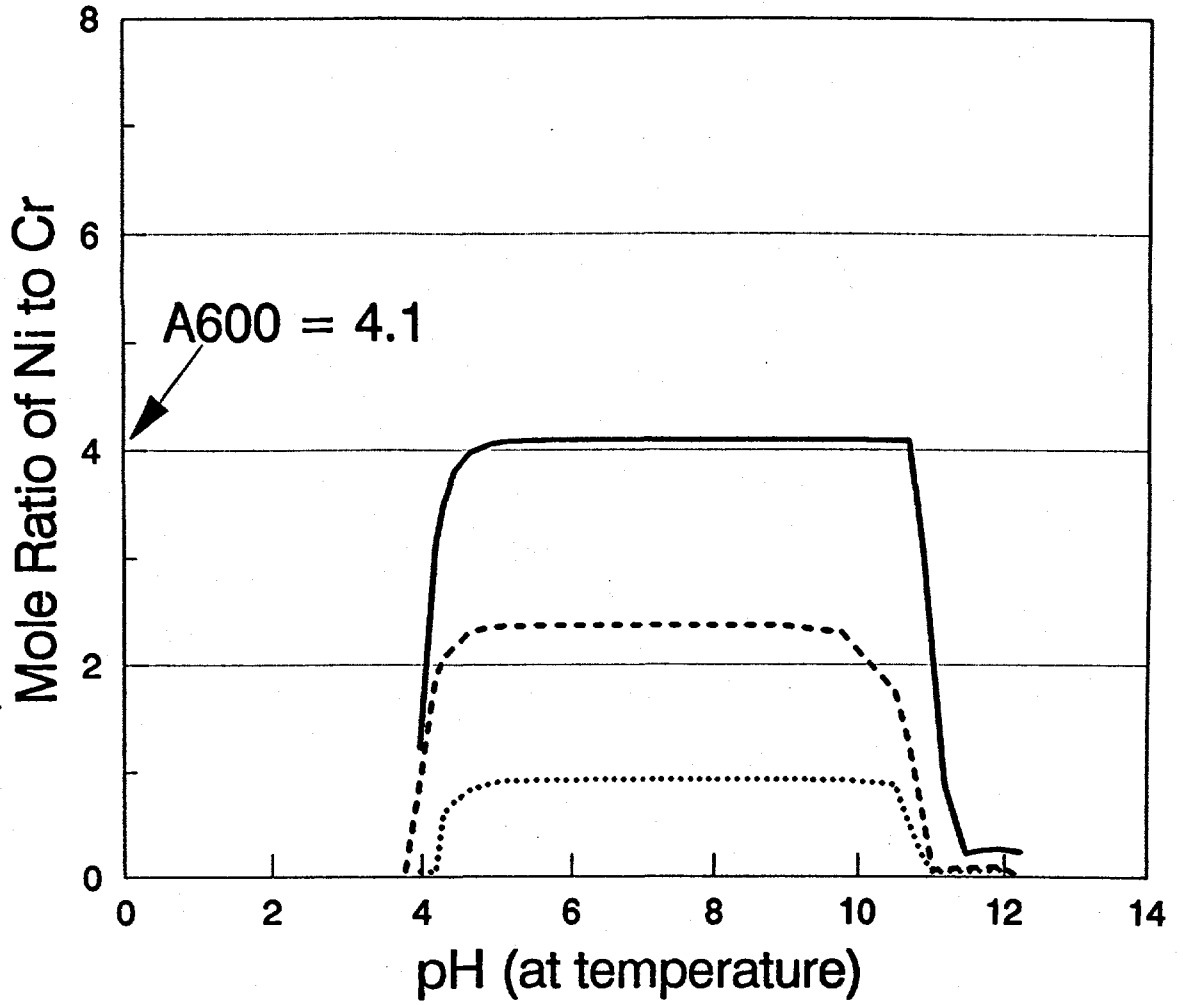


Figure (8)

Ni/Cr Ratio of Stable Oxides of Alloy 600

MULTEQ, Temperature = 315 C
(pH was adjusted with Na and Cl)



Initial Alloy Concentration
(Input to MULTEQ)

———— 6.79E-4 m

- - - - 1.36E-3 m

..... 2.04E-3 m

Figure (9)

Deposit Morphology of a Crack

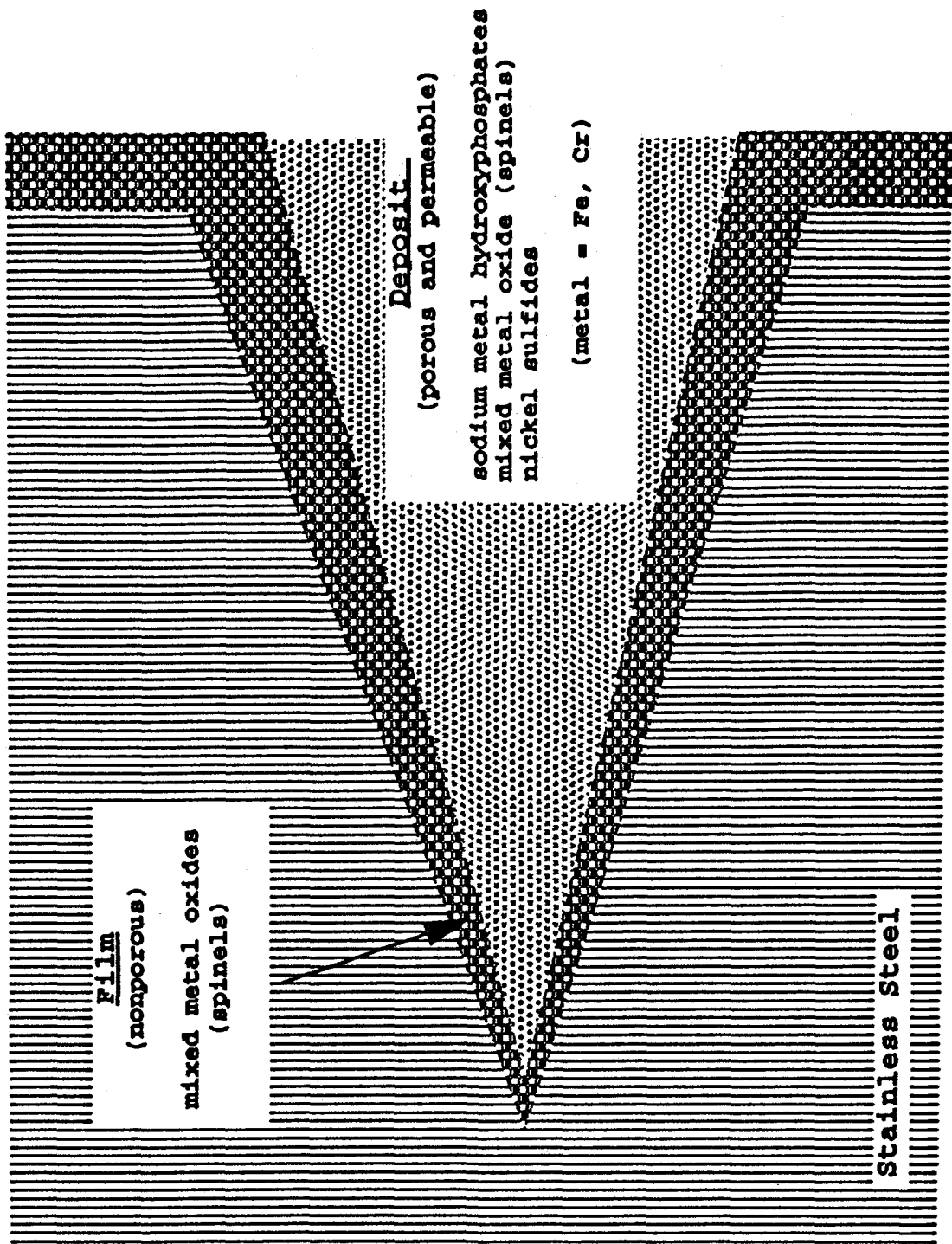


Figure (10)

Procedure for Nonuniform Crack Chemistry

(MULTEQ Coupled to Transport Model)

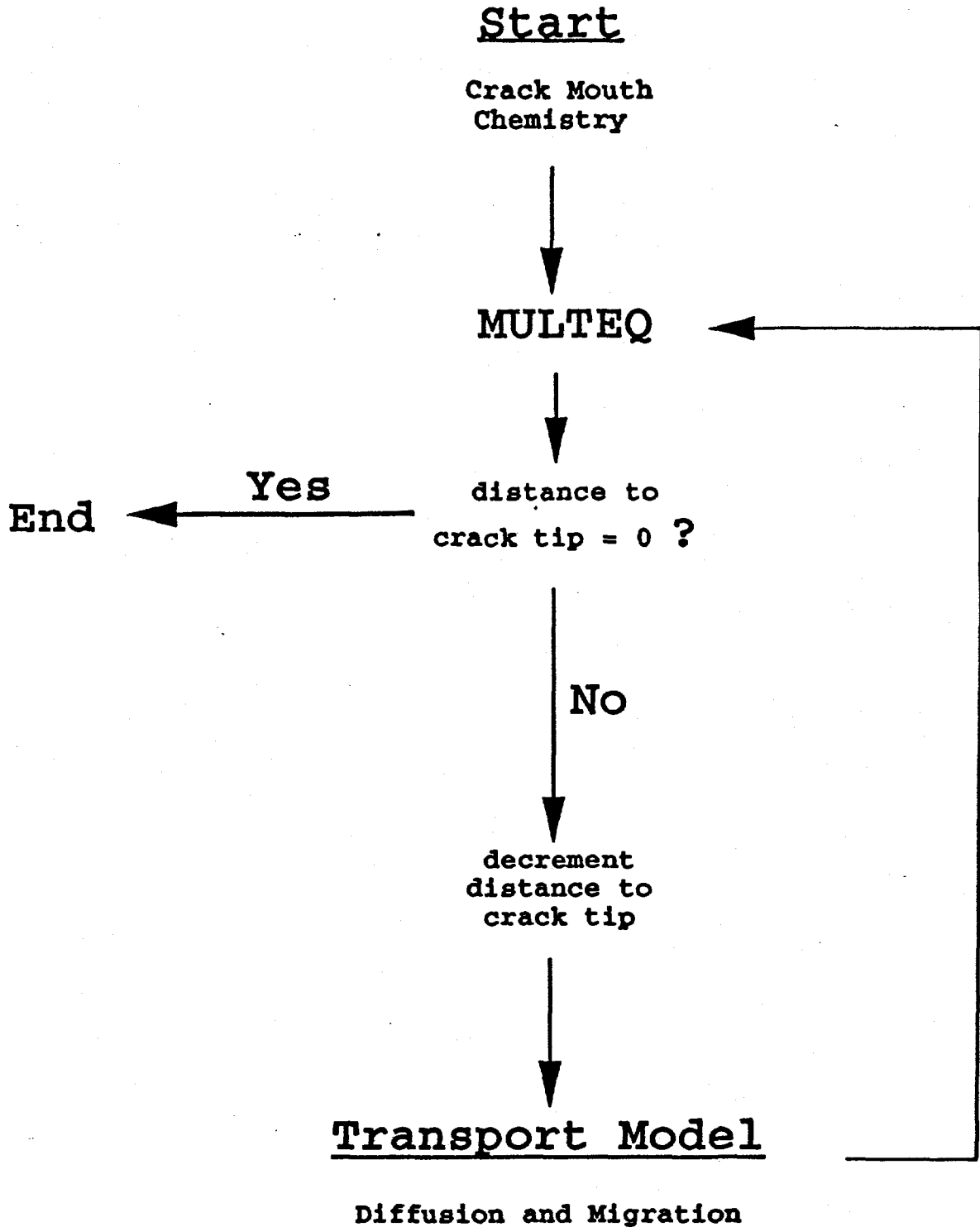


Figure (11)

Microanalysis Summary

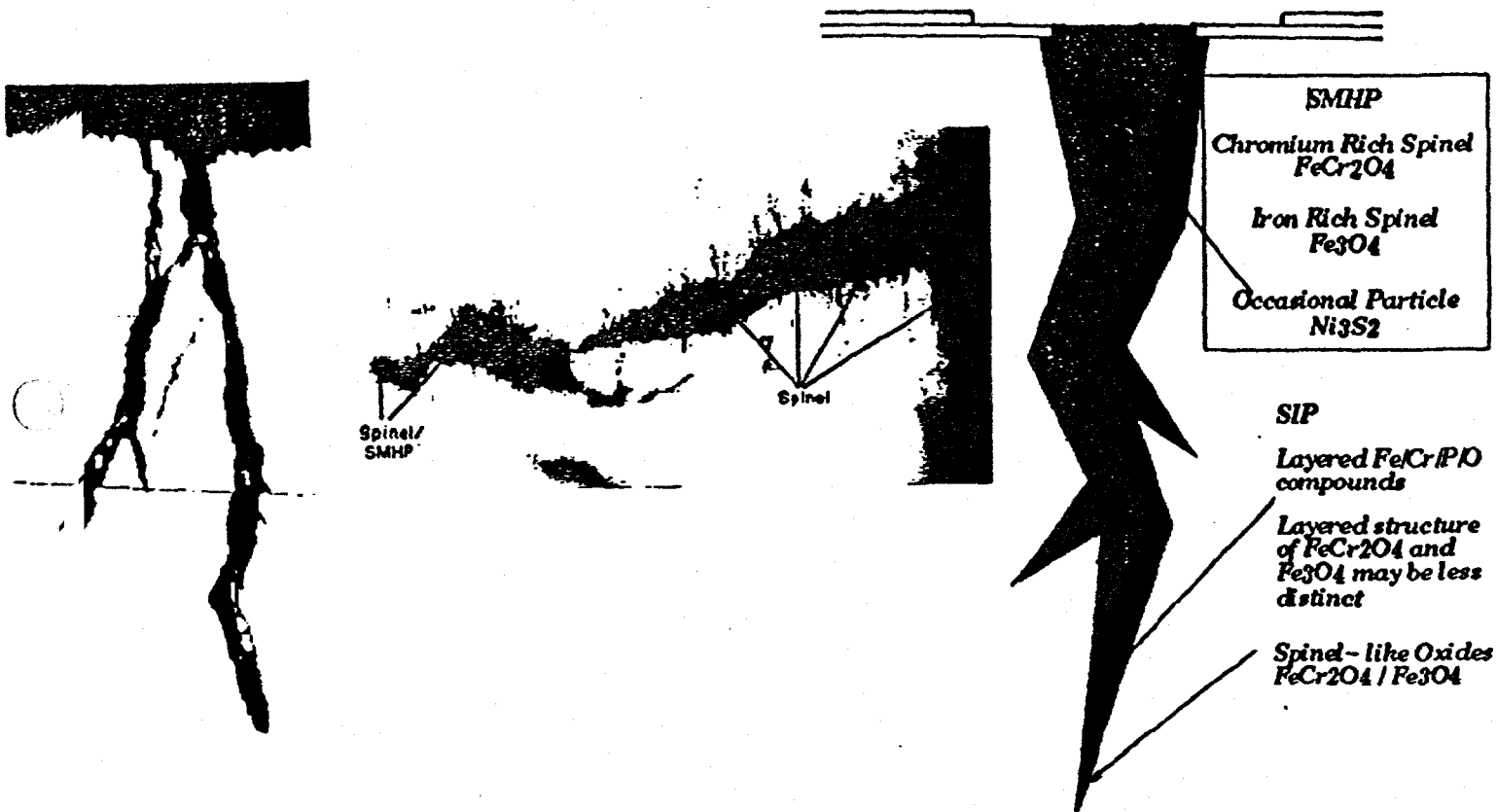


Figure (12)

**Chemical Gradients Produced by Flux of M^{+2} from Dissolving Metal Surface
(Pure Diffusion/Migration Transport, No Chemical Equilibrium)**

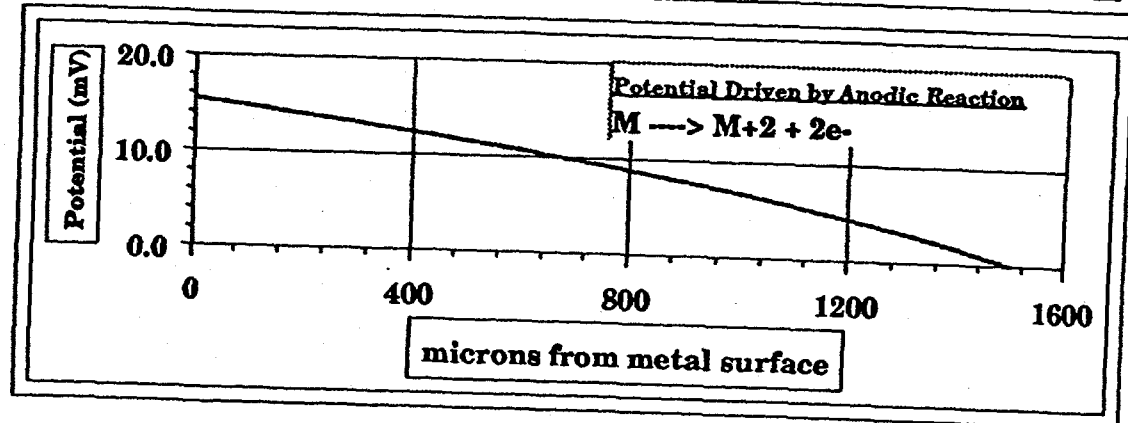
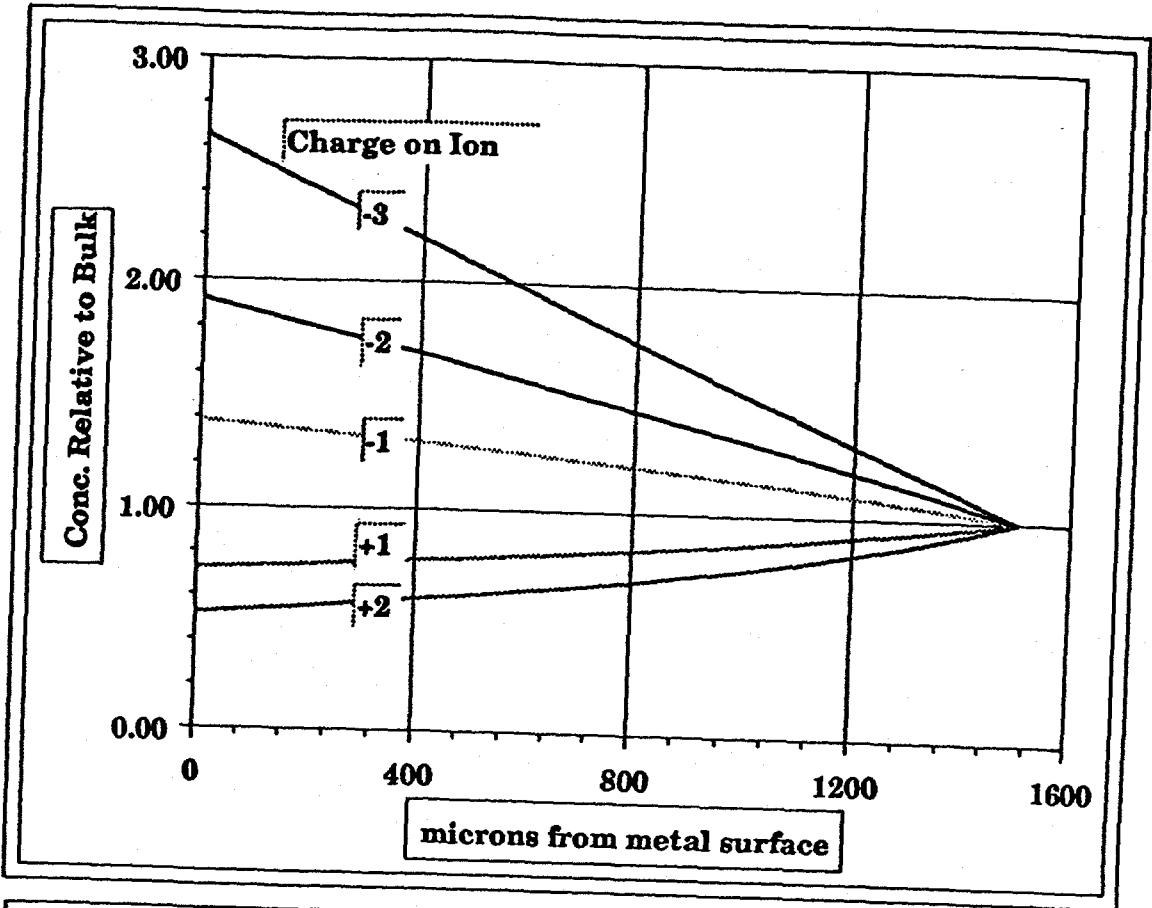


Figure (13)

Procedure for Nonuniform Crack Chemistry

(MULTEQ Coupled to Transport Model)

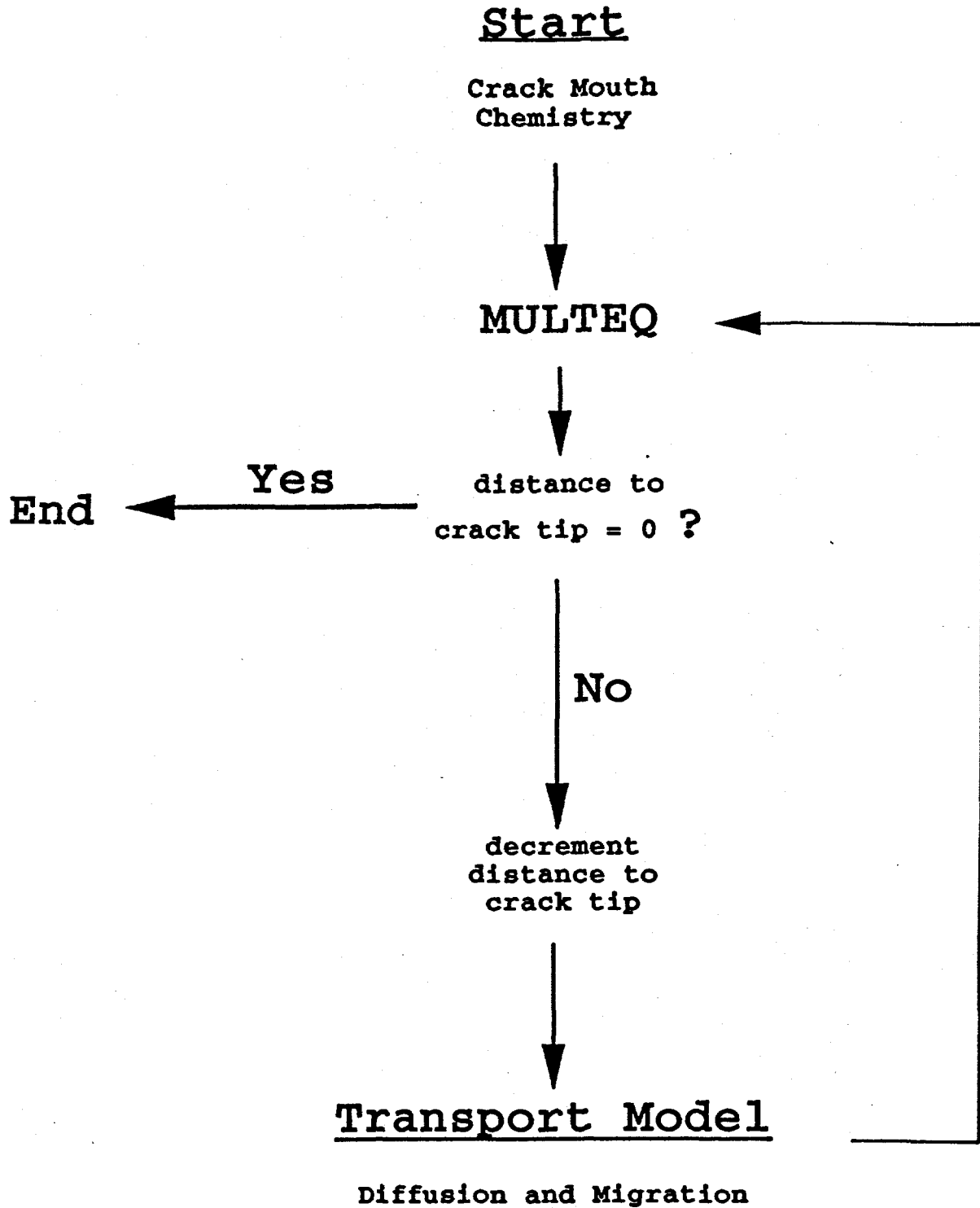


Figure (14)

Effect of Coupling MULTEQ to Diffusion and Migration Transport

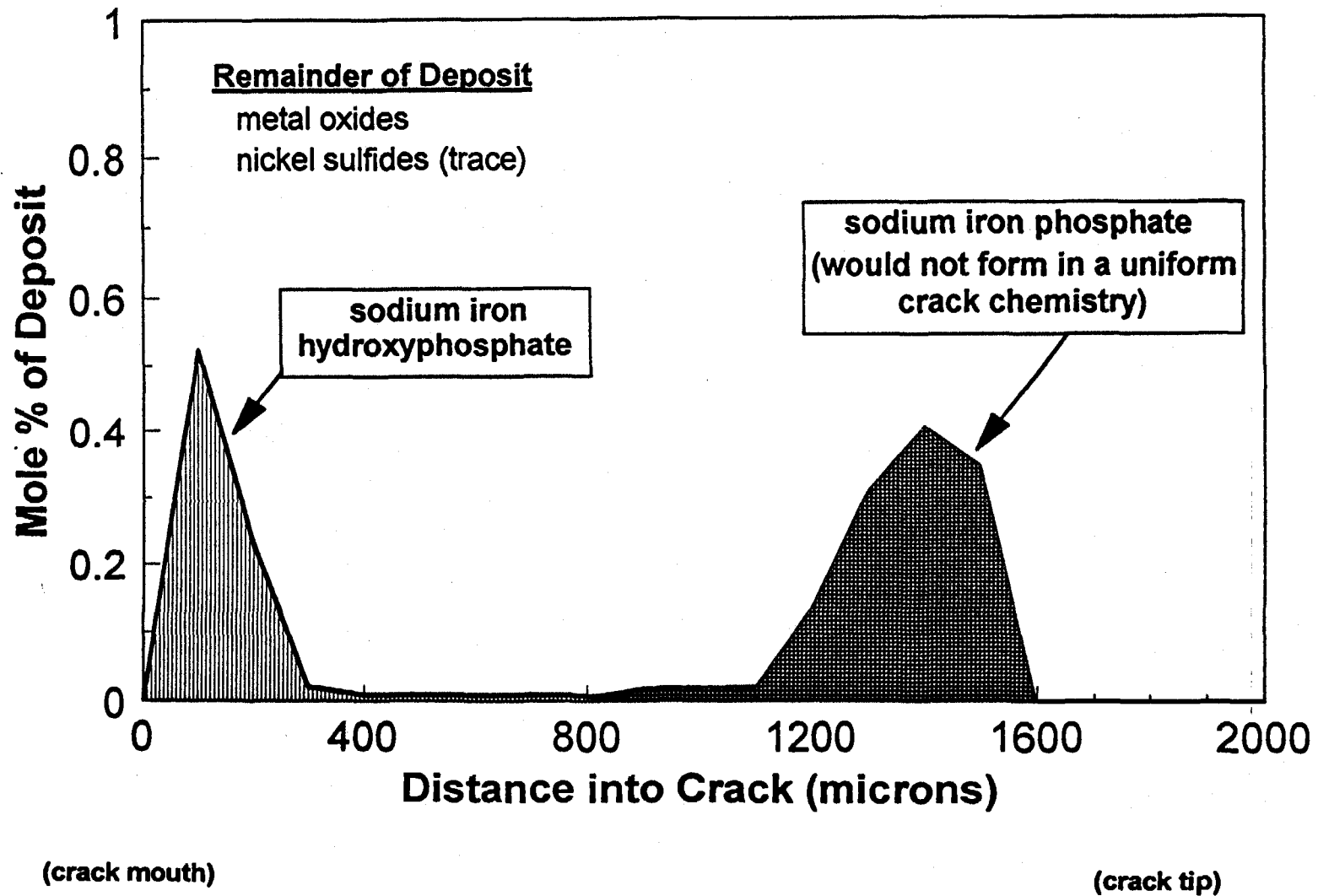
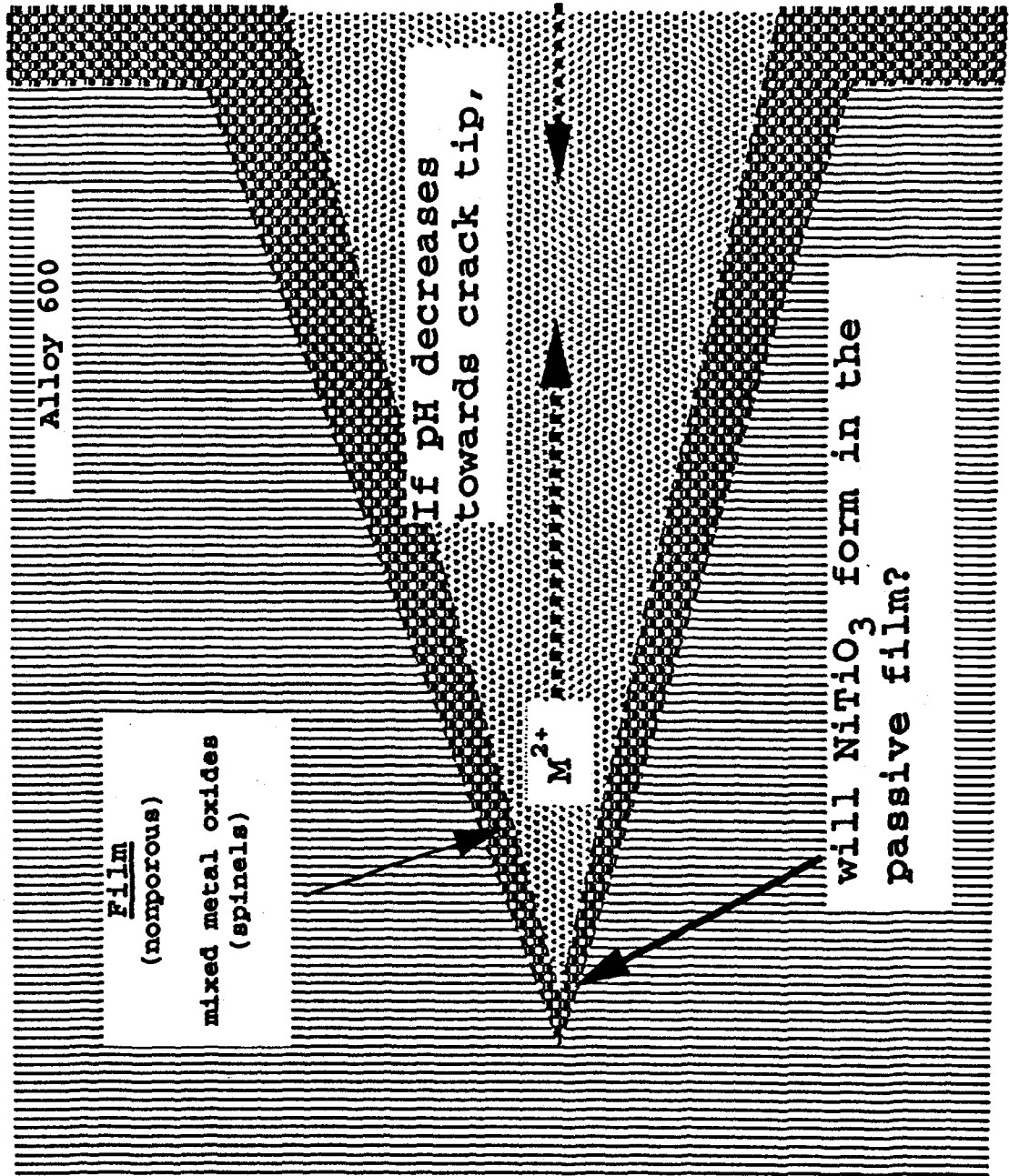


Figure (16)

Assess Effectiveness of TiO_2 Inhibitors



Bulk Chemistry

$Ti(OH)_5(H_2O)$