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Mr. Paul T. Day
Hanford Project Manager
U.S. Environmental Protection Agency
Region 10
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Richland, Washington 99352



Dear Mr. Day:

TRANSMITTAL OF THE GROUT TREATMENT FACILITY WHITE PAPER -- APPLICATION OF THE TOXIC CHARACTERISTIC LEACH PROCEDURE EXTRACTIONS FOR METALS TO HANFORD GROUTS

Transmitted herewith is the subject white paper. This white paper was requested by Mr. D. L. Duncan of the U.S. Environmental Protection Agency (EPA) at the February 18, 1993, Grout Unit Managers' Meeting. The paper describes the Westinghouse Hanford Company (WHC) concerns with using the standardized methods identified in SW 846.

While the white paper addresses the Toxic Characteristic Leach Procedure (TCLP) extract, we propose a total analysis with regulatory limits of 20 times concentrations listed in the table on Page 2.

Two main issues are discussed in this paper: sample size and sample spike recovery. Discussions with Mr. Duncan during the Unit Managers' Meeting indicated that experience in other mixed waste facilities showed that the radiological exposure associated with the required sample size and the ability to achieve the measurement limits of the Toxic Characteristic Leach Procedure with the smaller sample size was a problem. He also indicated that relief from the sample size requirements could be obtained. Dialogue regarding the sample spike recovery revealed that further discussion of this issue is required. The white paper provides that further discussion. It is requested that the EPA provide a formal determination on the alternatives proposed in this white paper.

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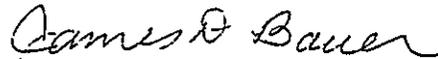
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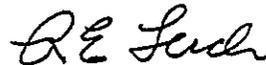
Should you have any questions regarding this transmittal, please contact Mr. C. E. Clark of the U.S. Department of Energy, Richland Field Office, on (509) 376-9333 or Ms. S. M. Price of WHC on 376-1653.

Sincerely,



James D. Bauer, Program Manager
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DOE Richland Field Office

EAP:CEC



R. E. Lerch, Deputy Director
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White Paper

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APPLICATION OF TCLP EXTRACTIONS FOR METALS TO HANFORD GROUTS

Introduction

The Toxic Characteristic Leach Procedure (TCLP) was designed by the Environmental Protection Agency (EPA) to evaluate the toxicity of a wide variety of waste based on the leachability of selected metals and organics under a closely controlled set of conditions. This report focuses on the TCLP testing for metals. The TCLP procedure used at the 222-S Laboratory to accommodate the radiological and chemical characteristics of Hanford grouted wastes may be considered to be outside the TCLP conditions found in the standard EPA procedure described in the Federal Register, Rules, and Regulations, Vol. 55, No. 61, Thursday, March 29, Appendix II, pp 11798-11877, and recently proposed in the third update (November 1990) of SW-846 procedures as Method 1311. The two major compliance concerns in the 222-S TCLP procedure are the use of smaller sample sizes, and the performance and evaluation of sample spikes. These concerns are based fundamentally on the radioactivity and high pH of the Hanford grouted waste. This report discusses these differences, and why they are not expected to affect the TCLP results.

TCLP Procedure

A general flow diagram for the TCLP procedure is provided in Figure 1. Before TCLP testing can begin several decisions must be made using preliminary testing to determine 1) if the weight percent solids exceed 0.5%; 2) if particle size reduction is required; and 3) which extraction fluid must be used. The grouted waste samples do not normally contain any liquids after the 28-day curing time, and therefore follow the 100% solids path in the flow diagram. Because the grouted sample specimens are single pieces larger than the 9.5 mm needed for the TCLP procedure, they are crushed to meet the TCLP particle size reduction requirement. A small sample of the crushed grout is tested to determine if extraction fluid #1 or #2 must be used. Extraction fluid #2 is used if the pH from this test is greater than 5. Because Hanford wastes normally contain large quantities of alkaline components that can neutralize the extraction fluid, it is not uncommon to see the more acidic (pH 2.08, 0.1 M H⁺) #2 fluid being used. The ratio of extraction fluid to solids is 20 to 1. After determining these factors 10 g (recommended sample size -100g) of the crushed grout, and 200 mL (recommended extraction volume - 2000mL) of the extraction fluid are added to an extraction vessel, and rotated for the prescribed speed and time. Before the extract is analyzed for the metals, it is filtered and the pH determined. If the TCLP procedure was followed according to Step 8.2.1 of Method 1311, two aliquots of the extract would be taken at this point, and one of the aliquots spiked with known quantities of the metals. The validity of spiking the extract at this point is one of the areas discussed below. Each of the extraction aliquots are then preserved by acidifying to pH <2 with nitric acid. The proposed alternative spiking Point #1 is after the acid preservation step. After the extract is preserved, it may be analyzed for metals using standard inductively coupled plasma (ICP) optical emission spectroscopy, or atomic absorption (AA) methods. Mercury is determined by cold vapor atomic absorption (CVAA) and is not digested by the same procedure as the other metals. Before the extracts can be analyzed, they must be digested in acid according to standard procedures. The preferred alternative spiking point is before the acid digestion step,

because it will measure losses and interferences that are caused by the analytical procedure, and not the extract chemistry. After the acid digestion, the extracts are analyzed by ICP and AA methods to determine the metal concentrations (mg/L) in the TCLP extract.

These results are used to determine if a waste exhibits the characteristic of toxicity by comparing the concentration of the contaminant in the leach solution to the regulatory level. The regulatory levels for the 8 toxic metals of interest are provided below:

Arsenic	(As)	-	5.0 mg/L
Barium	(Ba)	-	100.0 mg/L
Cadmium	(Cd)	-	1.0 mg/L
Chromium	(Cr)	-	5.0 mg/L
Lead	(Pb)	-	5.0 mg/L
Mercury	(Hg)	-	0.2 mg/L
Selenium	(Se)	-	1.0 mg/L
Silver	(Ag)	-	5.0 mg/L

If the analyte result is < 80% of the regulatory limit, and the spike recovery is > 50 %, no additional testing is necessary to show that the result is below the regulatory limit. However, if the analyte result is > 80% of the regulatory limit, or if the spike recovery is < 50%, and the result is below the regulatory limit then the method of standard additions (MSA) must be applied to the extract for that analyte. In the Method of Standards Addition (MSA) procedure, internal calibration in the sample matrix is done by taking four aliquots, and adding increasing known amounts of standard to three of the aliquots. The fourth aliquot does not contain a spike. The four aliquots are digested and analyzed using the normal ICP and atomic adsorption (AA) procedures. The results are then analyzed by linear regression, and the concentration of the analyte in the sample is equal to the "X" intercept. The purpose of the MSA procedure is to correct the result for analytical method matrix interferences. In the description of the MSA in the TCLP procedure, it is not clear at what point the spikes are added to the extract; however, it is assumed that they are added to aliquots of preserved extract during acid digestion, because any unpreserved extract would not be a valid sample.

TCLP Sample Size

The TCLP procedure is not explicitly clear on the required sample size for the test. The TCLP procedure indicates in some Sections (7.1, 7.1.5, 7.2, 7.2.1, and 7.2.5) that a minimum sample size of 100g is required. However, Section 7.2 for metal extraction also states that, "A minimum sample size of 100 grams (solid and liquid phases) is recommended." It further states that, "Enough solids should be generated for extraction such that the volume of TCLP extract will be sufficient to support all the analyses required." This rationale is also discussed in Section 7.1.5 and 7.2.5. A recent draft guidance document (Clarification of RCRA Hazardous Waste Testing Requirements for Mixed Waste, dated March 1992) jointly issued by the U.S. Nuclear Regulatory Commission (NRC) and the EPA to assist mixed waste generators in testing required by Resource Conservation and Recovery Act (RCRA) states, "The TCLP recommends a minimum sample size of 100 grams (Section 7.2), but sample sizes of less than 100g can be used if the result is that the test is still sufficiently sensitive, and can measure the constituents of interest at the regulatory

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levels prescribed by the Toxic Characteristic (TC)." The detection limits for the ICP and AA methods used are about 100 times lower than the TCLP limits. This allows smaller sample sizes and dilutions of the extract to be measured at regulatory levels. Based on this recent guidance, the smaller sample sizes probably are not an issue, but should be recognized by the regulatory agencies involved.

The 100 gram sample size requirement appears to be concerned with wastes that may contain significant quantities of liquid where insufficient amounts of solids may result in insufficient amounts of extract for analysis because of the 20:1 ratio of extraction fluid to solids requirement. This is not the case with grout samples which are 100% solid. Because the TCLP extract is only being used to analyze for metals, and the method sensitivity exceeds the regulatory requirement, the scaled down extraction volume (200 mL) for the 10 g sample is adequate for performing these tests.

Another potential reason for the 100 g sample size is to ensure that a representative sample of the waste is obtained. This large sample size may have been specified partly because the TCLP test is applied to many types of waste; many of which are very heterogenous. The grout waste form is prepared from a blending operation which ensures a relatively homogenous product. Replicate specimens of grouted waste are also prepared and analyzed which add credibility to the homogeneity of the specimen and reproducibility of the test.

In addition to the above justifications, there are some laboratory operational reasons for using smaller sample sizes. Larger sample sizes mean higher exposure to personnel from radioactive materials. The larger sample size also means that a larger percentage of samples would have to be prepared and extracted in the hot cell facilities rather than in hoods. This reduces sample throughput and efficiency, and consumes valuable hot cell space that is needed for other operations.

There are also operational problems associated with using the large sample size in the hot cell. A 100 g sample requires a 2000 mL extractant volume. The size and weight of the extractant container are difficult to handle with remote manipulators. In addition, the extraction apparatus and 2000 mL bottles take up large amounts of limited hot cell space. A small extraction apparatus that uses 200 mL bottles for extraction was fabricated by an EPA recommended manufacturer, Associated Design and Manufacturing Company, and is being used for TCLP on radioactive materials such as grout and single-shell tank wastes.

Matrix Spikes for TCLP Analyses

The purpose of the matrix spikes is to monitor the performance of the analytical methods used (ICP and AA) and to determine whether matrix interferences exist (Section 8.2.3). If the spike recovery is < 50%, the method is considered to be inadequate for evaluating, if results are below regulatory levels and additional analyses (four point method of standard additions) are required to substantiate the results. The point at which spikes are added in the standard TCLP procedure can result in low spike recoveries even though the analytical procedure does not have a matrix interference.

Section 8.2.1 of the procedure states that, "Matrix spikes are to be added after filtration of the TCLP extract and before preservation". This step also points out that spikes should not be added prior to TCLP extraction of the sample. Section 8.2 states, "As a minimum, follow the matrix spike addition guidance provided in each analytical method".

There are two alternative locations at which the matrix spikes could be added which would provide a more accurate evaluation of the analytical matrix effects on the TCLP results: 1) after preservation with nitric acid; and 2) during the acid digestion of the extract before analysis. The second alternative is the preferred location because it is the least sensitive to potential chemical reactions between the spike and the extract that can result in low spike recoveries.

Spiking the extract after filtration and before preservation with acid makes the spike recovery a function of the extract chemistry and not just the analytical method. The purpose of the spike is to evaluate if all of the metals are recovered from the acid digestions, and if there are any suppressive matrix interferences for the ICP and AA spectroscopic measurements that could lead to a false negative results. When the metal spikes are added to the extract before acidification, chemical reactions can occur that will result in precipitation of some of the metals. When aliquots are removed from these spiked containers for acid digestion, these trace precipitates of spikes will not be a part of the sample analyzed and low recoveries will result. These low recoveries are not caused by the analytical method, but by chemical reactions between the spike and the extraction fluid (extract chemistry) which results in subsampling inaccuracies.

This effect may be more significant for TCLP extracts that do not remain acidic, but have a final pH >7. This is a highly probable situation for Hanford wastes that contain many constituents that can neutralize acid such as hydroxide, aluminate, carbonate, phosphate, and nitrite. Under these alkaline conditions, the heavy metals (Cd, Pb, Ag, Cr(III), and Hg) can form insoluble hydroxides that may or may not redissolve when the extract is adjusted to pH < 2 during the preservation step. In addition to the formation of insoluble hydroxides, other insoluble compounds such as BaSO₄, AgCl, HgCl₂, or insoluble phosphates may form even in acidic solutions. Some spikes such as Cr(VI) may be stable in the basic solution, but precipitate when the acid is added because of reduction to Cr(III) by the nitrite ion. Similar oxidation/reduction reactions could occur with As and Se spikes. If the spike recoveries are low because of these reactions, the use of the method of standard additions will not improve the quality of the results or the accuracy of the decision, because MSA only evaluates the analytical method. Limited experience with the TCLP procedure on Hanford single-shell tank waste in which spikes were added before and after preservation indicate that some spike elements are lost because of these type of reactions. When the spikes are added during the acid digestion of the extract, good recoveries are obtained indicating that there are no significant interferences in the analytical method.

The first alternative point for spiking is after preserving the extract at pH < 2. Spiking at this point would help to minimize the formation of insoluble hydroxides; however, the formation of other insoluble compounds such as BaSO₄ and AgCl are still possible under acid conditions. Therefore, the

spike recoveries are still a function of the extract chemistry and not just the analytical method.

The second alternative point for adding the spike is at the acid digestion step. This is the normal ("minimum") accepted method for running matrix spikes for ICP and AA methods. This approach minimizes the influence of the extract chemistry, because the digestion acid and oxidation conditions are rigorous enough to keep the spikes in solution. This is the laboratory's preferred place to add the spikes, because if the spike recovery is poor at this point, then the required method of standards addition may produce a more valid result for comparison to the regulatory limit.

Conclusion

The proposed modifications to the TCLP procedure for testing Hanford grouts should not impact the ability to make accurate decisions concerning the wastes Toxic Characteristic using the TCLP. Recent regulatory guidance for mixed wastes indicates that the use of smaller sample sizes for the TCLP are acceptable. The reduced sample size does not impact the detection limit capability of the method needed to meet regulatory limits, and an adequate volume of extract should be available to complete all the metal tests. The smaller sample size offers significant operational advantages and reduces personnel radiation exposure.

The possibility of false negatives caused by the analytical method can be evaluated more accurately by spiking the extract at the acid digestion stage of analysis. Spiking the extract before or after preserving the TCLP extract with acid can result in low spike recoveries caused by precipitation reactions in the extract matrix, which cannot be corrected by using the method of standard additions.

FIGURE 1 - PROCEDURE FLOW FOR TCLP METALS EXTRACTION ON GROUT

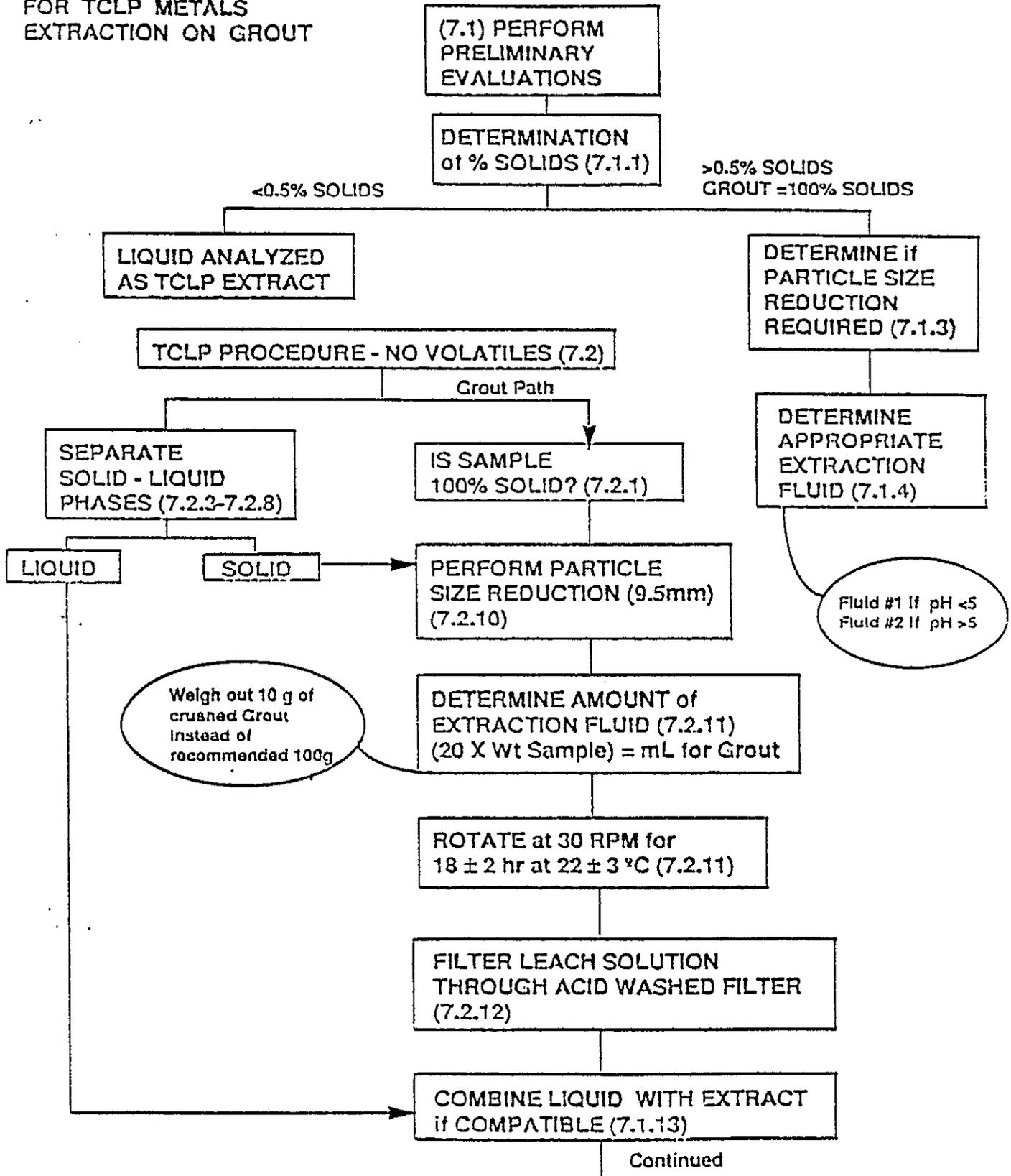
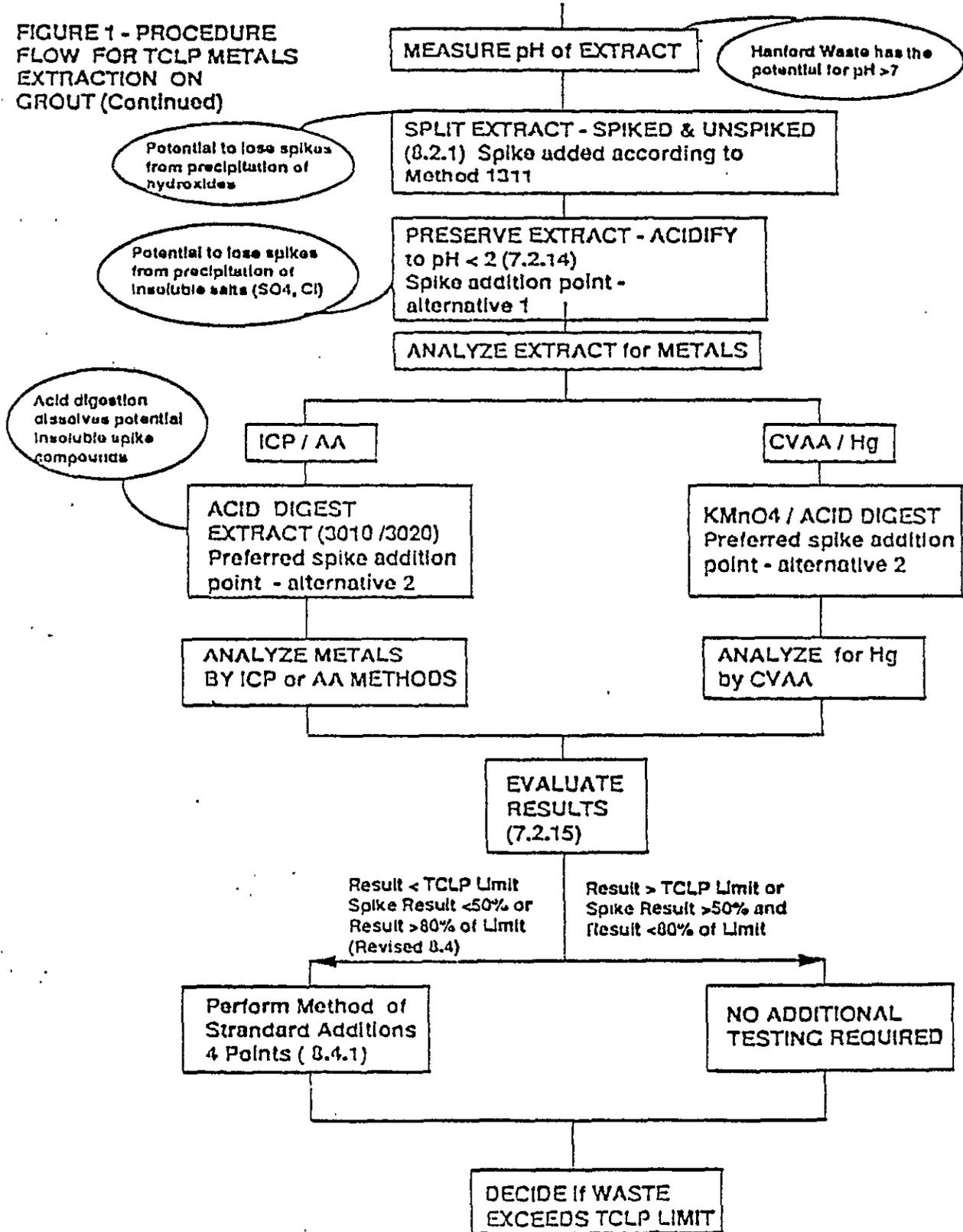


FIGURE 1 - PROCEDURE
FLOW FOR TCLP METALS
EXTRACTION ON
GROUT (Continued)



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