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SANDIA NATIONAL LABORATORIES
WASTE ISOLATION PILOT PLANT

AP-166
Revision 1

Analysis Plan for the Compilation and Testing of an EQ3/6 Database Incorporating New Pitzer and Other Thermodynamic Data

Task 4.4.2.2.1

Effective Date: December 15, 2014

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1 *Introduction and Objectives*

1.1 Introduction

This analysis plan guides the addition of thermodynamic parameters derived under AP-154 and AP-155 to a current quality assured EQ3/6 thermodynamic database with the ultimate creation of three new QA EQ3/6 thermodynamic databases. Because the timing of the completion of the tasks under AP-154 and AP-155 do not coincide it will be necessary to create three QA databases, the first of which will include the majority of the parameters derived under AP-154, and the second, which will build off of the first by the inclusion of the AP-155 derived parameters, and the remaining AP-154 parameters will be included in the third QA database. This analysis plan, as per NP 9-1, is considered a compliance decision analysis.

1.2 Objectives

The objective of this analysis plan is to create three verified QA EQ3/6 thermodynamic databases which include the parameters derived under AP-154 and AP-155 by using the currently verified QA EQ3/6 thermodynamic database, DATA0.FMT.R2, as the starting database. Since the tasks under AP-154 and AP-155 will not be completed simultaneously three verified QA databases will be created under this analysis plan. The first database, which will include the majority of the AP-154 derived parameters will be called DATA0.FMT.R3. The second QA database created by incorporating the AP-155 derived parameters will use DATA.FMT.R3 as the starting point, and adding the newly derived parameters to this database to create a new quality assurance approved thermodynamic database called DATA0.FMT.R4. A third QA database, DATA0.FMT.R5, will incorporate the remaining parameters derived under AP-154.

2 Approach

This AP outlines the procedure for the creation of three QA EQ3/6 thermodynamic databases, each of which builds on a previous QA database. Because of the timing of the availability of experimental data under the test plans, TP 08-02 and TP 10-01, it will be necessary to create three QA databases. The general procedure in doing so includes the creation and testing of interim databases, and final QA approval of the database. Below are described the methods for database creation using the data derived under AP-154 and AP-155.

The QA database that will include the majority of AP-154 derived parameters will be called DATA0.FMT.R3, the QA database that will be constructed from the AP-155 data will be DATA0.FMT.R4, and third QA database to be created will be called DATA0.FMT.R5 and it will include the remaining AP-154 derived parameters.

In the case of DATA0.FMT.R3 the approach that will be used in creating the new QA database will include the creation of two preliminary databases both of which will be based on the current QA database, DATA0.FMT.R2, testing of the preliminary databases, combining the two

databases into a single interim database, testing of the interim database, and finally issuing the QA database, DATA0.FMT.R3. A flowchart of the process is depicted in Figure 1.

Parameters derived under all tasks of AP-155 will be added to DATA0.FMT.R3 and tested to insure consistency. Figure 2 shows the methodology that will be used in the creation of DATA0.FMT.R4.

Due to the timing the hydrogen sulfide experiments under TP 08-02 the third QA database, DATA0.FMT.R5, will be created. This QA database will be built by adding parameters to DATA0.FMT.R4 and tested in accordance with Figure 3.

Testing of the preliminary databases will consist of spot checking the databases by running a few selected Python scripts from specific AP-154 and AP-155 tasks to insure consistency of the derived parameters. The choice of which Python scripts to run for testing will be based on those systems which use the greatest number of added and derived parameters. If discrepancies are encountered during testing, then the parameters derived under AP-154 or AP-155 may need to be reevaluated and the pertinent documentation revised.

The preliminary databases used to construct DATA0.FMT.R3 will be created based on the parameter groups iron complexes and lead complexes as well as supporting complexes that contain neither iron nor lead, but which were also derived under AP-154 (Table 1). The breakdown of which AP-154 derived parameter included in DATA0.FMT.R3 is listed in Table 1. Note that the AP-154 task numbers correspond to the TP 08-02 task numbers, and not all of the TP 08-02 tasks were analyzed under AP-154, due to factors such as concentration limits, or other experimental/analytical constraints as noted in Table 1.

Table 1.

AP-154 Task	Description	Justification	Database
1	Pitzer binary interaction parameter of $FeOH^+$—SO_4^{2-}	Included	DATA0.FMT.R3
2	Pitzer binary interaction parameter of $FeOH^+$— CO_3^{2-}	Included	DATA0.FMT.R3
3	Pitzer binary interaction parameter of $FeOH^+$—HS^-	Included	DATA0.FMT.R5
4	Pitzer binary interaction parameter of Fe^{2+}—HS^-	Included	DATA0.FMT.R5
5	Pitzer binary interaction parameter of Na^+—$Fe(OH)_3^-$	Included	DATA0.FMT.R3
6	Pitzer binary interaction parameter of Mg^{2+}—$Fe(OH)_3^-$	Included	DATA0.FMT.R3

AP-154 Task	Description	Justification	Database
7	Pitzer λ parameter of Na^+—FeOx(aq)	Included	DATA0.FMT.R3
8	Pitzer λ parameter of Mg^{2+}—FeOx(aq) Pitzer λ parameter of Na^+ — MgOx(aq)	Included	DATA0.FMT.R3
	Pitzer λ parameter of Mg^{2+} — MgOx(aq)	Delayed, will be included at later date	DATA0.FMT.R5
8	Pitzer λ parameter of Cl^- — MgOx(aq)	Excluded, data used to verify the use of MgOx/Na and MgOx/Mg pairs.	
9	Pitzer λ parameter of Cl^-—FeOx(aq)	Excluded, data used to verify the use of FeOx/Na and FeOx/Mg pairs.	
10	Pitzer binary interaction parameter of Na^+—$FeEDTA^{2-}$	Included	DATA0.FMT.R3
11	Pitzer binary interaction parameter of Mg^{2+}—$FeEDTA^{2-}$	Included	DATA0.FMT.R3
12	Pitzer binary interaction parameter of Na^+—$FeCit^-$	Included	DATA0.FMT.R3
13	Pitzer binary interaction parameter of Mg^{2+}—$FeCit^-$	Included	DATA0.FMT.R3
14	Pitzer binary interaction parameter of $PbCl^+$—HCO_3^-	Included	DATA0.FMT.R3
15	Pitzer binary interaction parameter of $PbCl^+$—CO_3^{2-}	Included	DATA0.FMT.R3
16	Pitzer binary interaction parameter of $PbCl^+$—SO_4^{2-}	Excluded, very low concentration, impact to system is negligible.	
17	Pitzer binary interaction parameter of $PbCl^+$—HS^-	Included	DATA0.FMT.R5
18	Pitzer binary interaction parameter of Na^+—$PbEDTA^{2-}$	Included	DATA0.FMT.R3

AP-154 Task	Description	Justification	Database
19	Pitzer binary interaction parameter of Mg^{2+}—$PbEDTA^{2-}$	Included	DATA0.FMT.R3
20	Pitzer binary interaction parameter of Na^{+}— $PbCit^{-}$	Included	DATA0.FMT.R3
21	Pitzer binary interaction parameter of Mg^{2+}— $PbCit^{-}$	Included	DATA0.FMT.R3
22	Pitzer λ parameter of Na^{+}—PbOx(aq)	Included	DATA0.FMT.R3
23	Pitzer λ parameter of Mg^{2+}— PbOx(aq)	Included	DATA0.FMT.R3
24	Pitzer λ parameter of Cl^{-}—PbOx(aq)	Included	DATA0.FMT.R3
25	Pitzer binary interaction parameter of Na^{+}—HS^{-}	Included	DATA0.FMT.R5
26	Pitzer binary interaction parameter of Mg^{2+}—HS^{-}	Included	DATA0.FMT.R5
27	Pitzer mixing interaction parameter of Cl^{-}—HS^{-}	Included	DATA0.FMT.R5
28	Pitzer binary interaction parameter of Na^{+}—$CaCit^{-}$	Included	DATA0.FMT.R3
29	Pitzer binary interaction parameter of Na^{+}—$HEDTA^{3-}$	Included	DATA0.FMT.R3
30	Pitzer binary interaction parameter of Mg^{2+}—$HEDTA^{3-}$	Included	DATA0.FMT.R3
31	Determination of solubility constant of di-calcium ethylenediaminetetraacetic acid (Ca_2EDTA), $Ca_2C_{10}H_{12}N_2O_8$(s)	Included	DATA0.FMT.R3
32	Pitzer λ parameter of Na^{+} — CaOxalate(aq) Pitzer λ parameter of Mg^{2+} — CaOx(aq)	Included	DATA0.FMT.R3

AP-154 Task	Description	Justification	Database
	Pitzer λ parameter of Cl^- — CaOx(aq)	Cl^- — CaOx(aq) excluded from Task 32, data used in verification of another system.	
33	Pitzer binary interaction parameter Cl^- — $FeEDTA^{-2}$	Excluded, analytical measurement not available at time of this revision.	
34	Pitzer binary interaction parameter Na^+—$FeOH^+$	Excluded, no measurement possible because of the very low concentration.	
35	Pitzer binary interaction parameter Mg^{2+}—$CaCit^-$	Included	DATA0.FMT.R3
36	FeOx(aq) – Na^+ & Mg^{2+}	Excluded, data used to verify the use of FeOx/Na and FeOx/Mg pairs.	
37	Pitzer binary interaction parameter of Cl^-—$HEDTA^{3-}$	Excluded.	

Table 2 Tasks and parameters from AP-155, which will be added to DATA0.FMT.R3 in the creation of the QA database DATA0.FMT.R4.

Table 2.

AP-155 Task	Description	Justification	Database
1	Solubility constant of boracite	Included	DATA0.FMT.R4
2	Formation constant of $FeB(OH)_4^+$	Included	DATA0.FMT.R4
3	Formation constant of PbB_4O_7(aq)	Included	DATA0.FMT.R4
4.1	Pitzer binary interaction parameter of $PbB(OH)_4^+$—Cl^-	Included	DATA0.FMT.R4
4.2	Pitzer binary interaction parameter of $PbB(OH)_4^+$—SO_4^{2-}	Included	DATA0.FMT.R4
4.3	Pitzer binary interaction parameter of Na^+—$Pb[B(OH)_4]_3^-$	Included	DATA0.FMT.R4
4.4	Pitzer binary interaction parameter of Mg^{2+}—$Pb[B(OH)_4]_3^-$	Included	DATA0.FMT.R4
4.5	Pitzer binary interaction parameter of $MgB(OH)_4^+$—SO_4^{2-}	Included	DATA0.FMT.R4

AP-155 Task	Description	Justification	Database
4.6	Pitzer binary interaction parameter of $CaB(OH)_4^+$—SO_4^{2-}	Included	DATA0.FMT.R4
4.7	Pitzer λ parameter of Na^+—$NaB(OH)_4$(aq)	Included	DATA0.FMT.R4
4.8	Pitzer λ parameter of Mg^{2+}—$NaB(OH)_4$(aq)	Included	DATA0.FMT.R4
4.9	Pitzer ζ parameter of $NaB(OH)_4$(aq) with NaCl + $MgCl_2$	Included	DATA0.FMT.R4
4.10	Pitzer λ parameter of Na^+—PbB_4O_7(aq)	Included	DATA0.FMT.R4
4.11	Pitzer λ parameter of Mg^{2+}—PbB_4O_7(aq)	Included	DATA0.FMT.R4
4.12	Pitzer ζ parameter of PbB_4O_7(aq) with NaCl + $MgCl_2$	Included	DATA0.FMT.R4

Figure 1. Flow Chart for Incorporation AP-154 Parameters Into Database for Testing

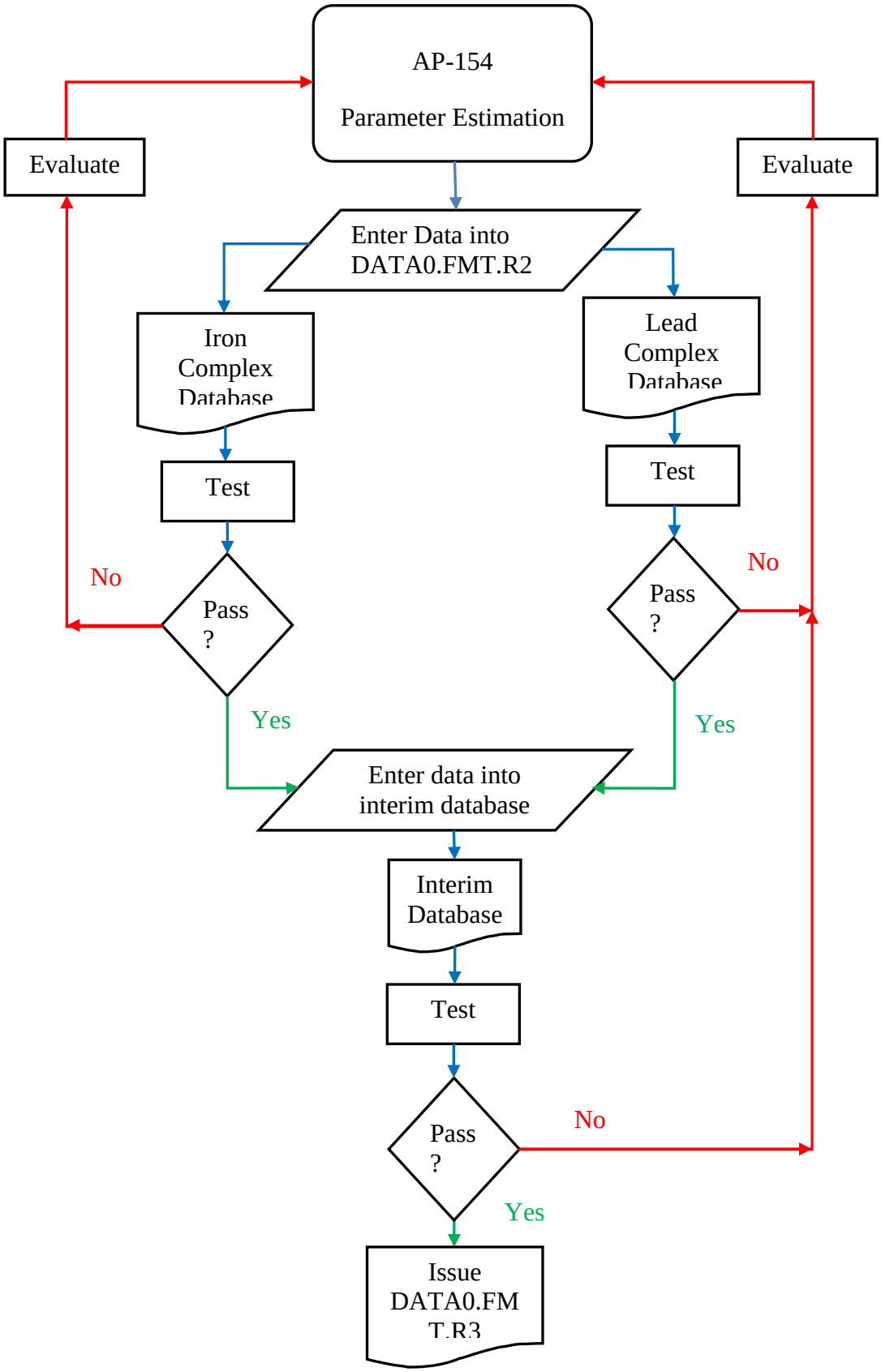


Figure 2. Flow Chart for Incorporation AP-155 Parameters Into Database for Testing.

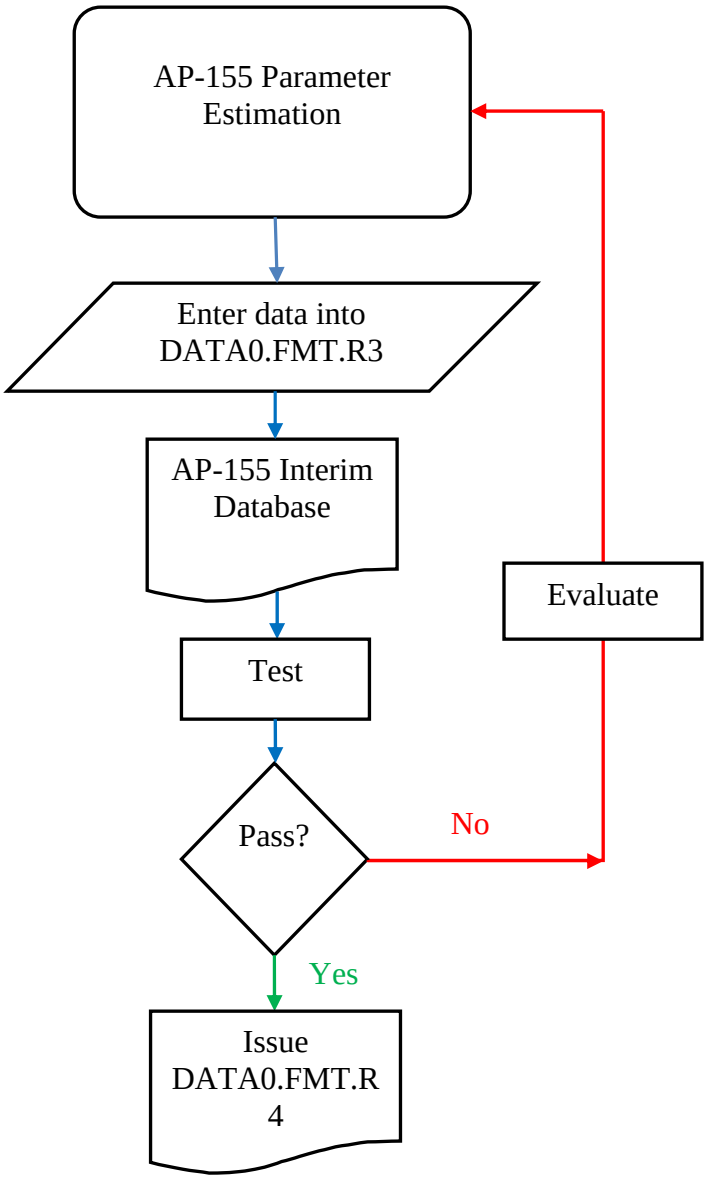
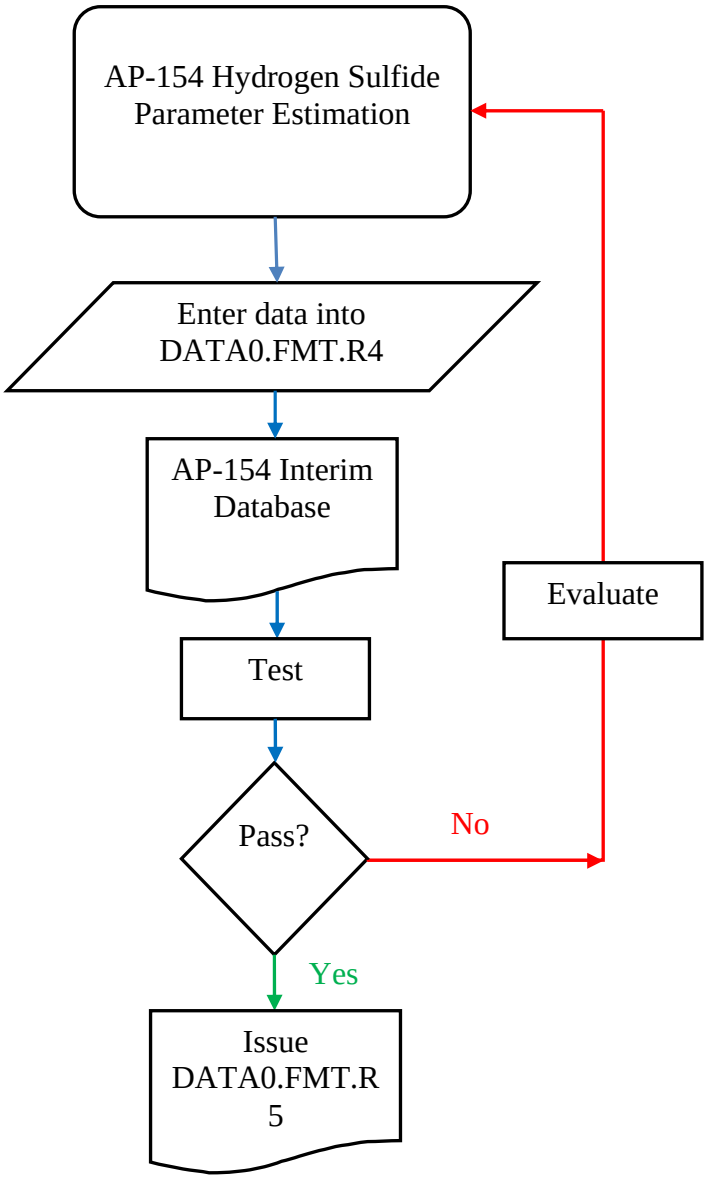


Figure 3. Flow Chart for Incorporation AP-154 Hydrogen Sulfide Parameters Into Database for Testing.



2.1 Software List

The software to be used is EQ3/6 Version 8.0a (Wolery and Jarek, 2003; Wolery, 2008; Wolery et al., 2010; Xiong, 2011b), and DATA0.FM1 (Xiong, 2011a). In addition, off the shelf software such as Microsoft Excel, and the Excel macro *GetEQData_v101f.xls* will be used to extract data from the EQ3/6 output files, and the open source text editor Notepad++ may be used to edit the preliminary and final databases.

2.2 Acceptance Criteria

During the testing phases of the preliminary and interim databases comparisons between fitted parameters and EQ3/6 output will be made in Microsoft Excel. Parameters and simulation output will be considered acceptable if they are they agree in the first three significant figures, i.e., variation in the third and greater significant figures will be considered acceptable.

3 Tasks

There are three primary tasks under this AP, each of which will result in the creation of a QA thermodynamic database. The subtasks for each task includes the creation of the preliminary databases, testing of the preliminary databases, evaluation of the test results, evaluation of errors and re-testing as necessary, and issuance of the final QA database(s). The creation and testing of the preliminary, interim, and final thermodynamic databases created during the execution of this AP will be summarized in memos that will be submitted to the WIPP Record Center. The final QA databases will be documented in an analysis report which will accompany the issuance of the three QA databases, DATA0.FMT.R3, DATA0.FMT.R4, and DATA0.FMT.R5.

Table 3 lists the tasks, database name, and completion date for AP-166. Each task corresponds to the creation of a QA database.

Table 3.

Task	Database	Completion Date
1	DATA0.FMT.R3	10/15/2015
2	DATA0.FMT.R4	04/15/2016
3	DATA0.FMT.R5	10/15/2016

Paul Domski will be the primary analyst performing the tasks under this AP, estimated dates for completion are contingent upon the completion of the tasks under AP-154 and AP-155. Therefore, it is expected that the final QA databases will be complete, a memo of notification will be issued to users, and the final database will be submitted to WIPP records to be stored in the CMS and/or the CVS with all accompanying documentation.

4 Special Considerations

Depending on the results of database testing it may be necessary to revise documents submitted under AP-154 and AP-155.

5 Applicable Procedures

All applicable WIPP QA procedures will be followed when conducting this AP.

- Training of personnel will be conducted in accordance with the requirements of NP 2-1, *Qualification and Training*.
- Analyses will be conducted and documented in accordance with the requirements of NP 9-1, *Analyses*.
- All software used will meet the requirements laid out in NP 19-1, *Software Requirements* and NP 9-1, as applicable.
- The analyses will be reviewed following NP 6-1, *Document Review Process*.
- All required records will be submitted to the WIPP Records Center in accordance with NP 17-1, *Records*.

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