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Permanent

Analysis of Solids Remaining Following Chemical Cleaning in Tank 6F

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February 5, 2010

Savannah River National Laboratory
Savannah River Nuclear Solutions
Aiken, SC 29808

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LIST OF ACRONYMS

ICPES	inductively-coupled plasma emission spectroscopy
ICPMS	inductively-coupled plasma mass spectroscopy
LWO	Liquid Waste Organization
SMP	Submersible Mixer Pumps
SRNL	Savannah River National Laboratory
SEM	Scanning Electron Microscopy
SRR	Savannah River Remediation
XRD	X-ray Diffraction

1.0 SUMMARY

Following chemical cleaning, a solid sample (i.e., process sample) was collected and submitted to Savannah River National Laboratory (SRNL) for analysis. SRNL analyzed this sample by X-ray Diffraction (XRD) and scanning electron microscopy (SEM) to determine the composition of the solids remaining in Tank 6F and to assess the effectiveness of the chemical cleaning process.

The conclusions from this work follow.

- The dominant species measured by XRD (in order) are hematite, maghemite, nickel oxalate hydrate, and goethite.
- Hematite and nickel oxalate hydrate are not easily dissolved by oxalic acid.
- The nickel oxalate spectra measured could include contributions from manganese oxalate or ferrous oxalate.
- The primary elements identified by the SEM analysis are iron, nickel, and oxygen.
- The particle size analysis showed the highest concentration of particles between 4 and 10 microns, but some particles were as large as 2,000 microns.

When combined with the chemical analysis of the Tank 6F sample, this data suggests that additional acid strikes are unlikely to remove a significant fraction of the remaining sludge mass.

2.0 INTRODUCTION

The first step in preparing the tank for closure is mechanical sludge removal. During mechanical sludge removal, Operations adds liquid (e.g., inhibited water or supernate salt solution) to the tank to form a slurry. They mix the liquid and sludge with pumps, and transfer the slurry to another tank for further processing.

Mechanical sludge removal effectively removes the bulk of the sludge from a tank, but is not able to remove all of the sludge. In Tank 6F, a sludge heel with estimated volume of 5,984 gallons remained after mechanical sludge removal.[1] To remove this sludge heel, SRR performed chemical cleaning. The chemical cleaning included two oxalic acid strikes, a spray wash, and a water wash.

Savannah River Remediation (SRR) conducted the first oxalic acid strike as follows. Personnel added 110,830 gallons of 8 wt % oxalic acid to Tank 6F and mixed the contents of Tank 6F with two submersible mixer pumps (SMPs) for approximately four days. Following the mixing, they transferred 115,903 gallons of Tank 6F material to Tank 7F. The SMPs were operating when the transfer started and were shut down approximately five hours after the transfer started. SRR collected a sample of the liquid from Tank 6F and submitted it to SRNL for analysis.[2] Mapping of the tank following the transfer indicated that 2,400 gallons of solids remained in the tank.

SRR conducted the second oxalic acid strike as follows. Personnel added 28,881 gallons of 8 wt % oxalic acid to Tank 6F. Following the acid addition, they visually inspected the tank and transferred 32,247 gallons of Tank 6F material to Tank 7F.[3] SRR collected a sample of the liquid from Tank 6F and submitted it to SRNL for analysis.[2] Mapping of the tank following the transfer indicated that 3,248 gallons of solids remained in the tank.

Following the oxalic acid strikes, SRR performed spray washing to remove waste collected on internal structures, cooling coils, tank top internals, and tank walls. The acid spray wash was followed by a water spray wash to remove oxalic acid from the tank internals. SRR conducted the spray wash as follows. Personnel added 4,802 gallons of 8 wt % oxalic acid to Tank 6F through the spray mast installed in Riser 2, added 4,875gallons of oxalic acid through Riser 7, added 5,000 gallons of deionized water into the tank via Riser 2, and 5,000 gallons of deionized water into the tank via Riser 7. Following the spray wash, they visually inspected the tank and transferred 22,430 gallons of Tank 6F material to Tank 7F.[4] SRR collected a sample of the liquid from Tank 6F and submitted it to SRNL for analysis.[2]

Following the spray wash and transfer, SRR added 113,935 gallons of well water to Tank 6F. They mixed the tank contents with a single SMP and transferred 112,699 gallons from Tank 6F to Tank 7F.[4] SRR collected a sample of the liquid from Tank 6F and submitted to SRNL for analysis.[2] Mapping of the tank following the transfer indicated that 3,488 gallons of solids remained in the tank.

Following the water wash, SRR personnel collected a solid sample and submitted it to SRNL for analysis to assess the effectiveness of the chemical cleaning and to provide a preliminary indication of the composition of the material remaining in the tank. That effort is described in another SRNL report.[5]

3.0 SAMPLES RECEIVED AND ANALYZED

SRNL received solid samples (process samples) FTF-06-09-27-1, FTF-06-09-27-2, and FTF-06-09-27-3 on May 12, 2009. The samples were brown colored and contained very little free liquid. We combined the samples and collected three sub-samples (Tank 6F Solid 1, Tank 6F Solid 2, and Tank 6F Solid 3) for analysis by XRD and another three subsamples (Tank 6F Sample 4, Tank 6F Sample 5, and Tank 6F Sample 6) for analysis by SEM.[6] The following pages show the spectra from the XRD analysis, SEM photos, and the elemental composition of spots on select particles.

4.0 RESULTS

4.1 XRD

Figures 1 - 3 show the spectra from the XRD analyses. On all three spectra, the compound present in highest concentration is hematite (Fe_2O_3), followed by maghemite (Fe_2O_3), nickel oxalate hydrate ($NiC_2O_4 \cdot 2H_2O$), and goethite (α-$Fe^{+3}O(OH)$). SRNL analysis of Tank Farm historical sludge samples shows the iron to be primarily magnetite (Fe_3O_4) and hematite according to Dr. Michael Hay. Literature indicates magnetite dissolves more readily in oxalic acid than hematite.[7] Since magnetite was not identified in these samples, we conclude that the magnetite dissolved in the oxalic acid cleaning. Since hematite is present and does not dissolve easily in oxalic acid, additional acid strikes may be ineffective in dissolving this compound. The analysis of liquid and solid samples collected during Tank 6F chemical cleaning showed the second acid strike, the spray wash, and the water wash removed no more than an additional 5%

of the available sludge mass. Additional acid strikes are unlikely to remove a significant fraction of the remaining sludge mass.[5]

A review of literature found nickel oxalate hydrate to form from the reaction of nickel salts with oxalic acid.[8] Therefore, nickel oxalate hydrate is likely to be present in Tank 6F. Additional oxalic acid strikes are unlikely to dissolve this compound. SRNL Analytical Chemists have postulated that the nickel compound identified could be an iron (II) or manganese compound, also.

A literature review found goethite to dissolve more readily in oxalic acid than hematite.[9] Additional oxalic acid strikes could dissolve the goethite, but are unlikely to dissolve the hematite.

The fifth compound is identified as plutonium oxalate hydrate ($Pu_2(C_2O_4)_3 \cdot 10H_2O$). This compound provided a good match to the spectra measured, but the concentration of plutonium in the solid samples (~ 100 mg/kg) is much below the detection limit for the XRD analysis. Therefore, SRNL Analytical Chemists have postulated that the fifth compound is an iron oxalate hydrate.

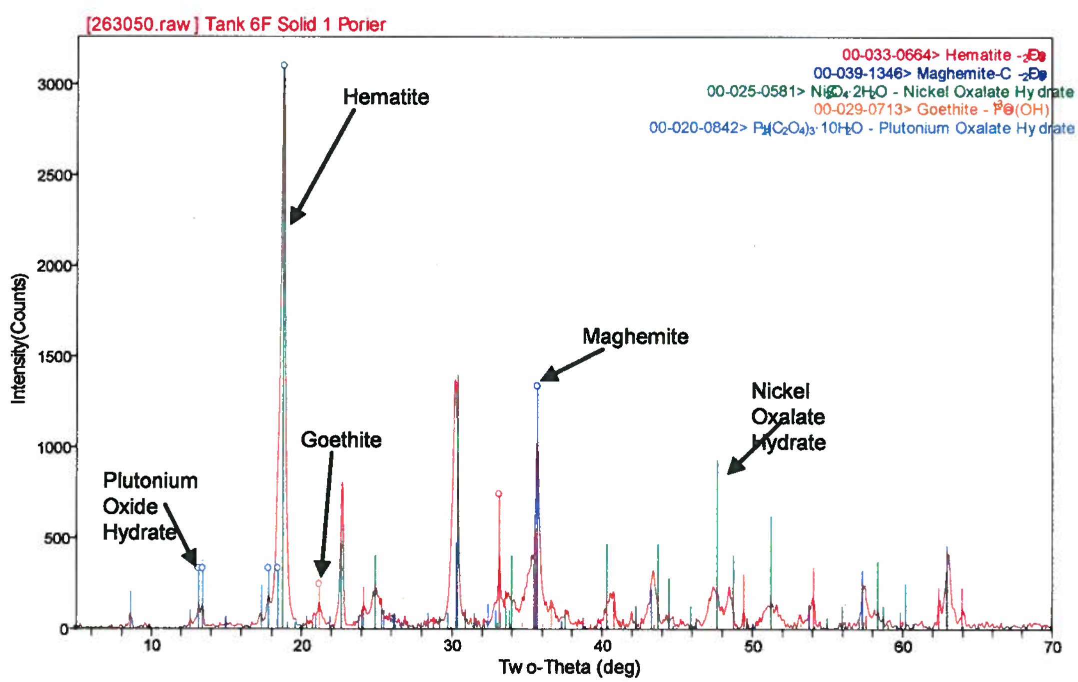

Figure 1. XRD Analysis of Tank 6F Solid Sample 1

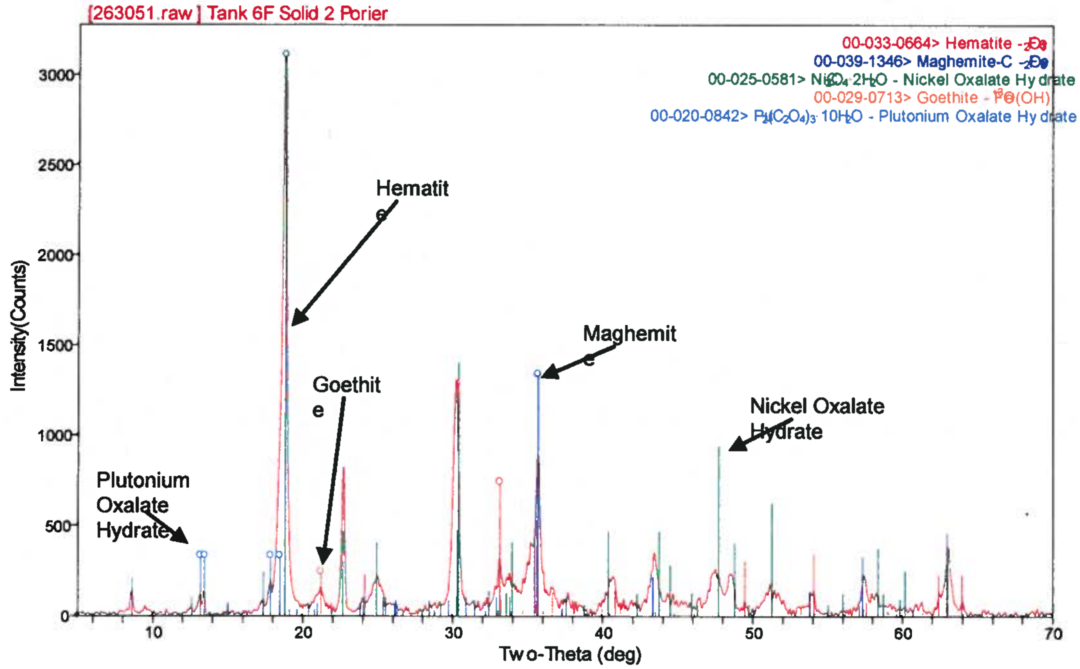

Figure 2. XRD Analysis of Tank 6F Solid Sample 2

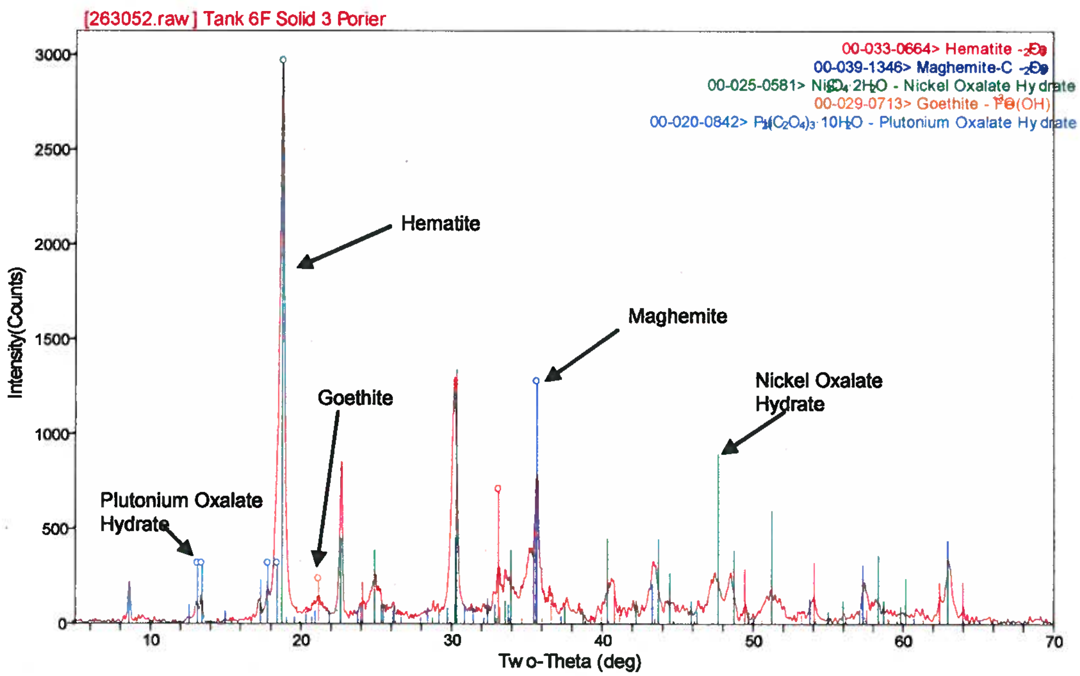

Figure 3. XRD Analysis of Tank 6F Solid Sample 3

4.2 SEM

The raster scan of Tank 6F Sample 4 (see Figure 10 and Figure 11) shows the dominant elements to be iron, nickel, and oxygen. The oxygen could be from oxalate or oxide compounds, as identified in the XRD analysis described previously. The scan shows lesser amounts of manganese, aluminum and silicon.

The scans of select spots from Tank 6F Sample 4 (see Figures 4 – 9 and Figures 12 - 22) show large amounts of iron, nickel, manganese, and oxygen. The scans show lesser amounts of aluminum and silicon. A few scans show molybdenum, sulfur, mercury, lead, barium, and copper. Two of the scans show cerium, neodymium, lanthanum, yttrium, and gadolinium.

The raster scan of Tank 6F Sample 5 (see Figure 28 and Figure 29) shows the dominant elements to be iron, nickel, and oxygen. The scan shows lesser amounts of manganese, aluminum silicon, and neodymium.

The scans of select spots from Tank 6F Sample 5 (see Figures 23 – 27 and Figures 30 – 37) show large amounts of iron, nickel, manganese, and oxygen. The scans show lesser amounts of aluminum and silicon. A few scans show molybdenum, sulfur, mercury, lead, barium, chromium, and tungsten. Two of the scans show cerium, neodymium, lanthanum, yttrium, and gadolinium.

The raster scan of Tank 6F Sample 6 (see Figure 42 and Figure 43) shows the dominant elements to be iron, nickel, and oxygen. The scan shows lesser amounts of manganese, mercury, aluminum and silicon.

The scans of select spots from Tank 6F Sample 6 (see Figures 38 – 41 and Figures 44 - 51) show large amounts of iron, nickel, manganese, and oxygen. The scans show lesser amounts of aluminum and silicon. A few scans show molybdenum, sulfur, mercury, palladium, and chloride. Two of the scans show cerium, neodymium, lanthanum, yttrium, and gadolinium.

The SEM analysis shows the dominant species to be iron, nickel, and oxygen. The inductively-coupled plasma emission spectroscopy (ICPES) analysis performed on these solid samples showed iron to be 53% of the measured cations and nickel to be 33 – 35% of the measured cations.[5] The oxygen could be from metal oxides or metal oxalates. The measured manganese in the Tank 6F solid sample was ~ 7% of the measured cations, so its presence in the SEM scans is expected. The measured mercury, aluminum, and silicon concentrations in the solid sample were 2.3%, 1.3 %, and 0.7 %, respectively. The other species observed were present at less than 1% in the Tank 6F solid samples. At concentrations less than 1%, these species will only be observed by SEM if the analyst selects spots containing these species for analysis. The measured uranium concentration in the Tank 6F solid sample was less than 1%. Because the SEM raster scans detect the particles in majority and uranium is a small fraction of the remaining solids, it would only be observed by SEM if a uranium-containing particle was selected by the analyst, and dwelled on exclusively by spot mode.

To estimate the particles size distribution of the Tank 6F insoluble solids, researchers used the backscattered electron images obtained from the SEM and analyzed these images with digital imaging software (Pixcavator, version 2.1). The SEM images were converted to black and white (using the Otsu algorithm in the software) to form a binary image. The size of the objects in the binary images was measured (using the Feret's tangent line method within the software) to determine the particle size distribution of the Tank 6F sludge sample. The calculated particle size (see Figure 52 and Figure 53) shows the highest concentration of particles between 4 and 10 microns (number basis) and between 1000 and 2000 microns (volume basis). With a particle density of 2 g/mL, a fluid density of 1 g/mL, and a fluid viscosity of 1 cp., 10, 100, and 2000 micron particles would settle at rates of 2 in/day, 185 in/day, and 74,000 in/day, respectively.

Tank 6F Sample 4

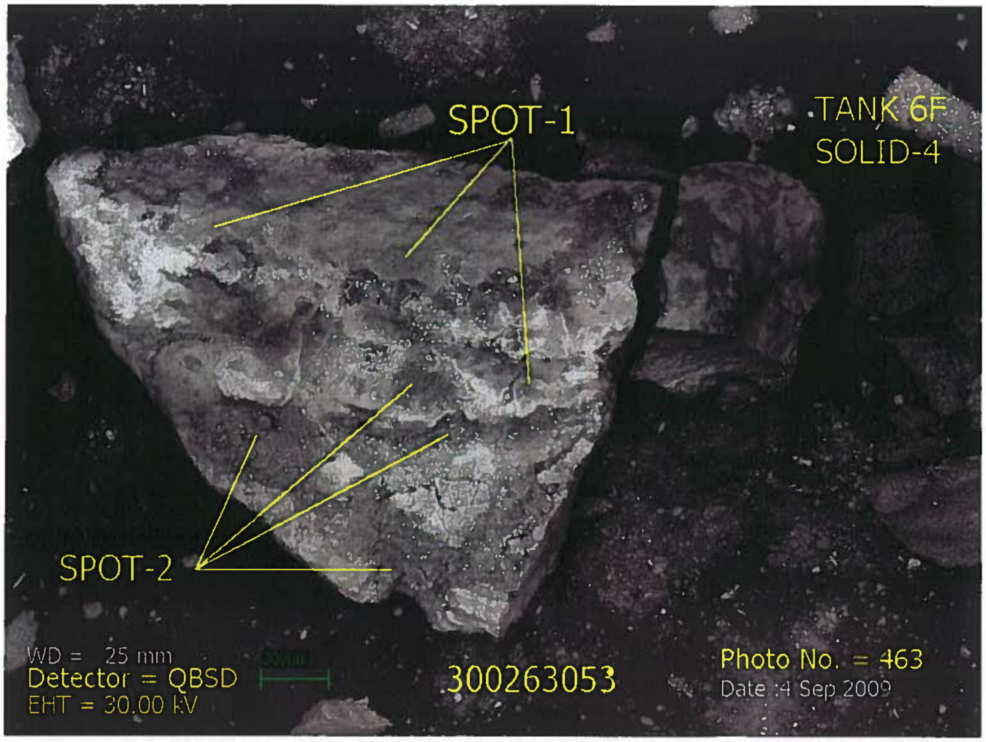

Figure 4. Tank 6F Sample 4 Spots 1 and 2

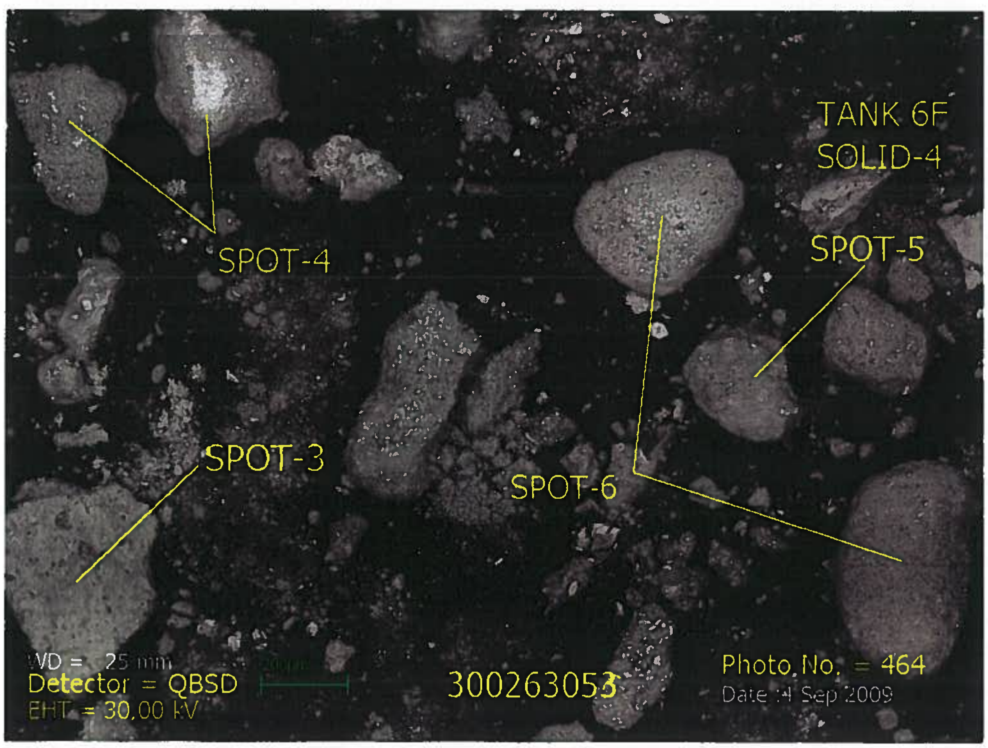

Figure 5. Tank 6F Sample 4 Spots 3 - 6

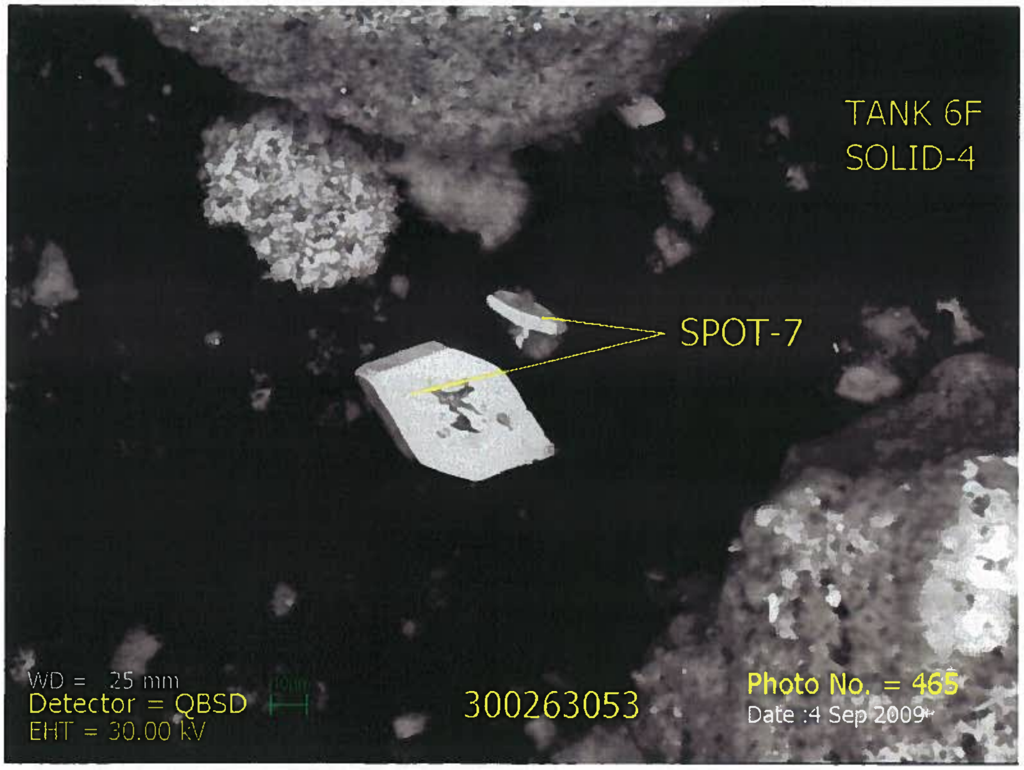

Figure 6. Tank 6F Sample 4 Spot 7

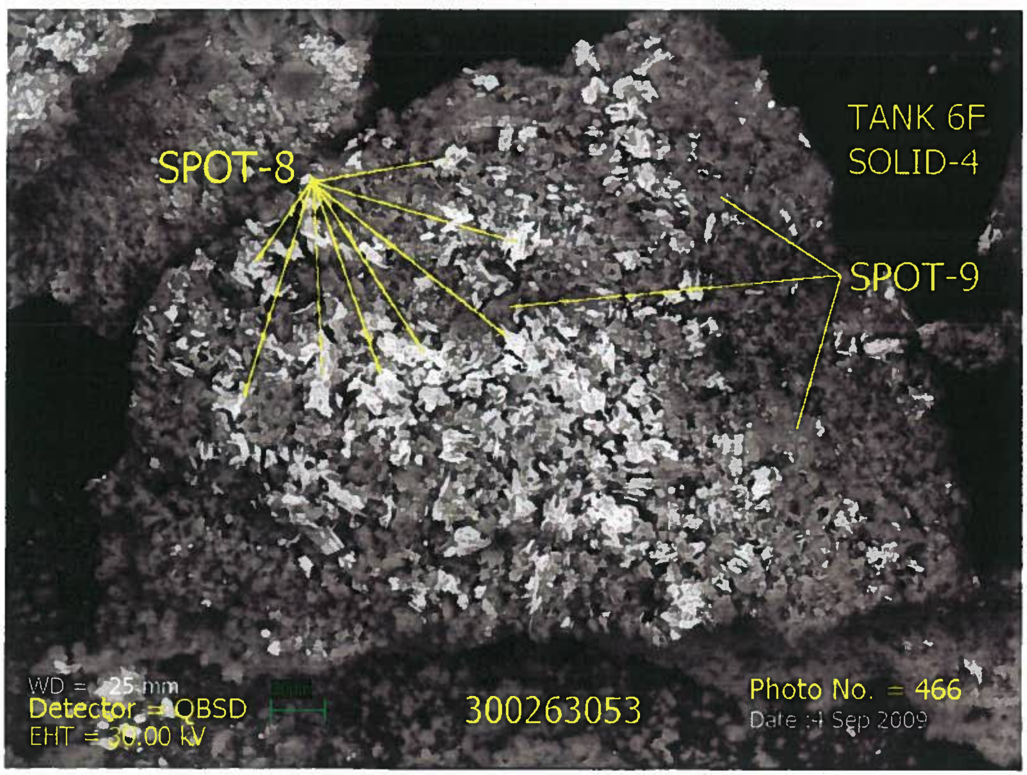

Figure 7. Tank 6F Sample 4 Spots 8 and 9

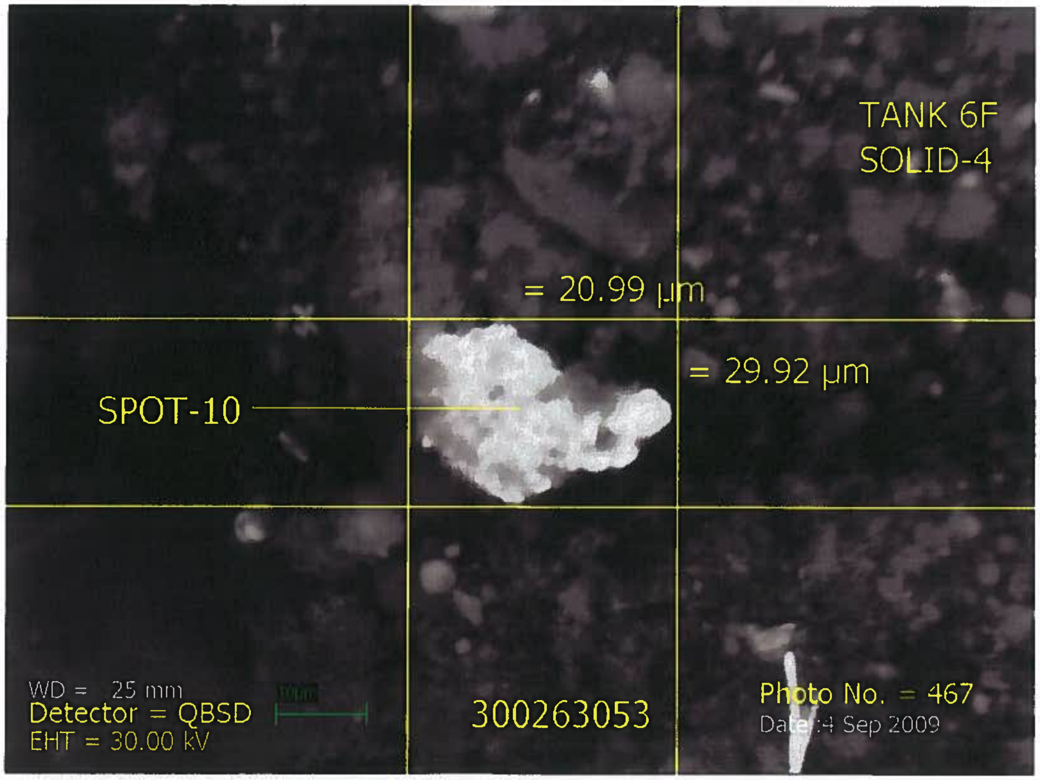

Figure 8. Tank 6F Sample 4 Spot 10

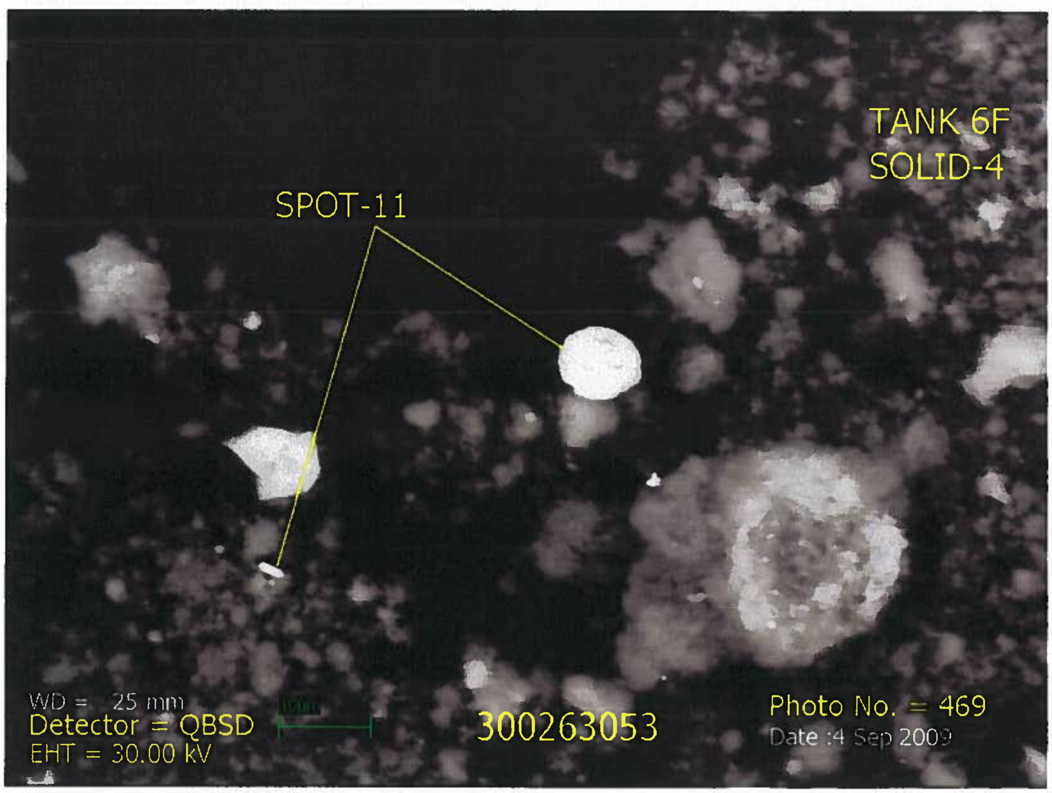

Figure 9. Tank 6F Sample 4 Spot 11

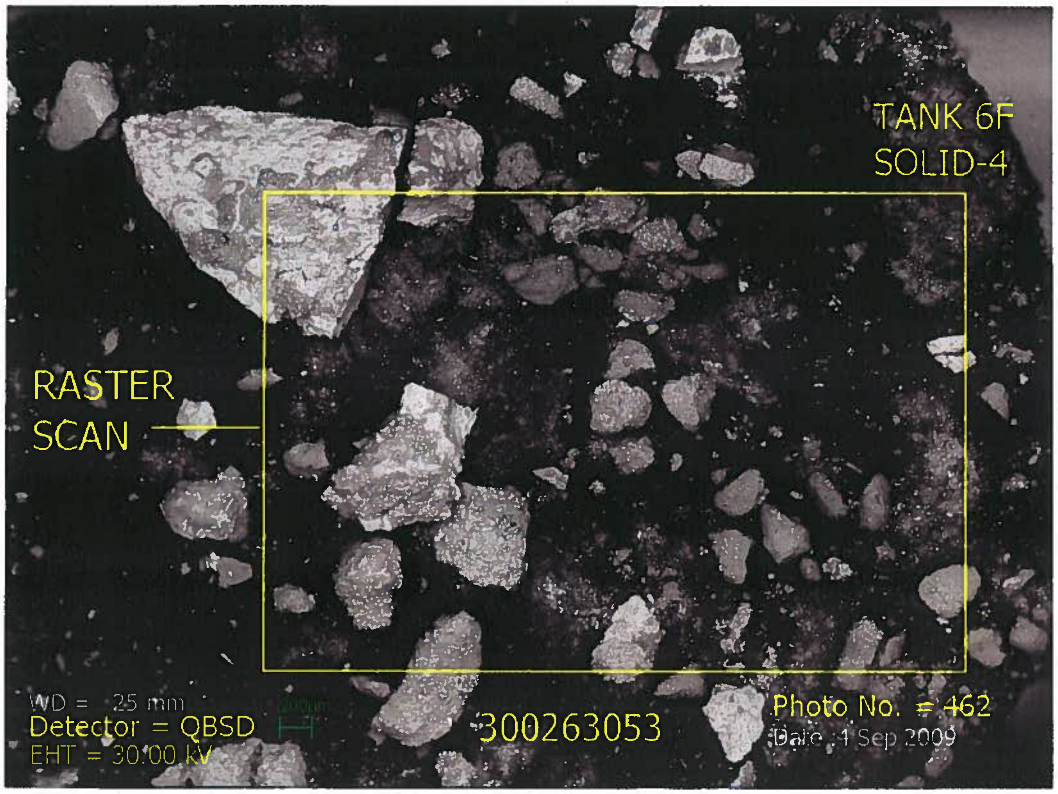

Figure 10. Tank 6F Sample 4 Raster Scan

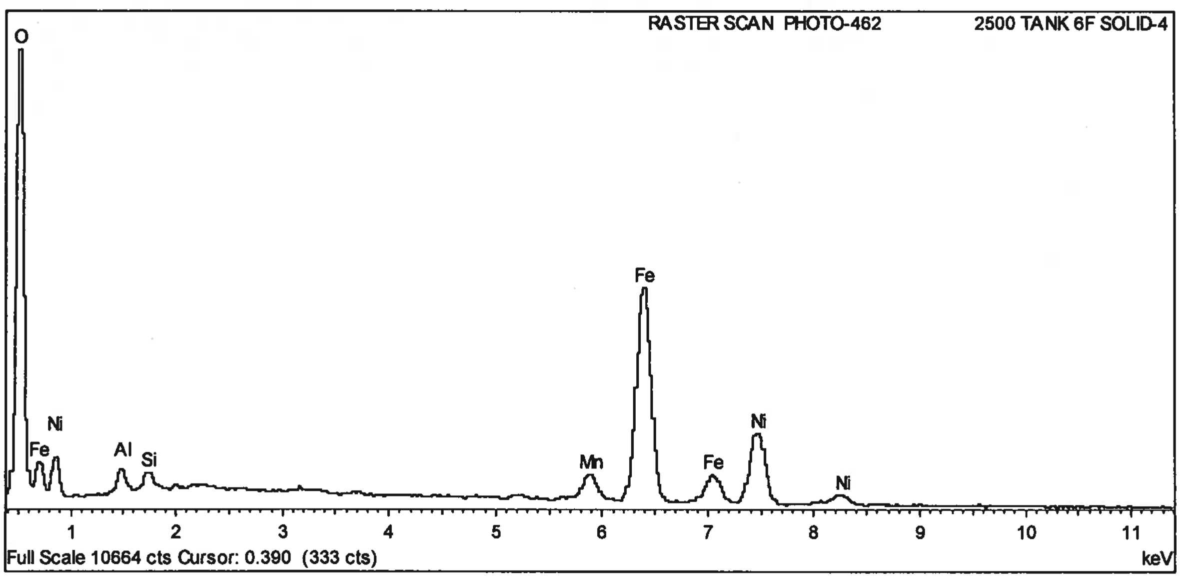

Figure 11. Tank 6F Sample 4 Raster Scan

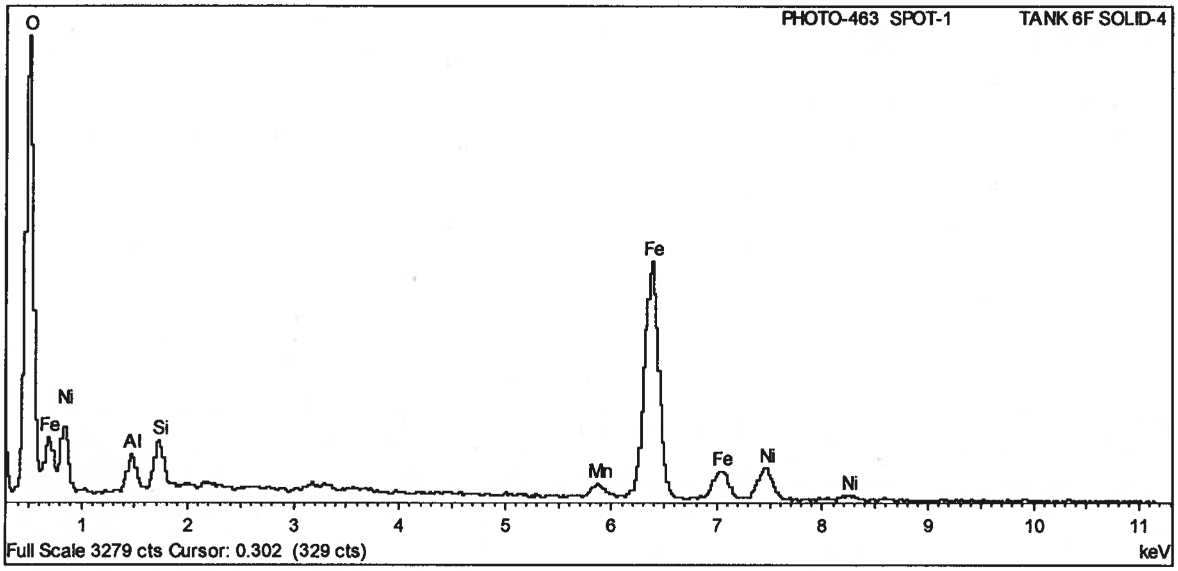

Figure 12. Tank 6F Sample 4 Spot 1

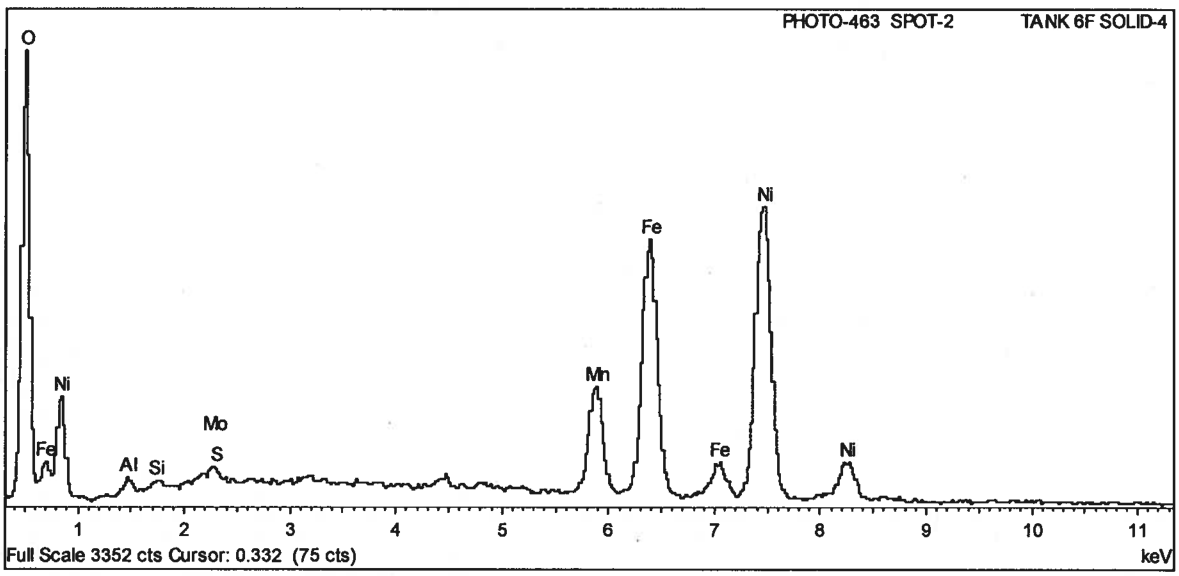

Figure 13. Tank 6F Sample 4 Spot 2

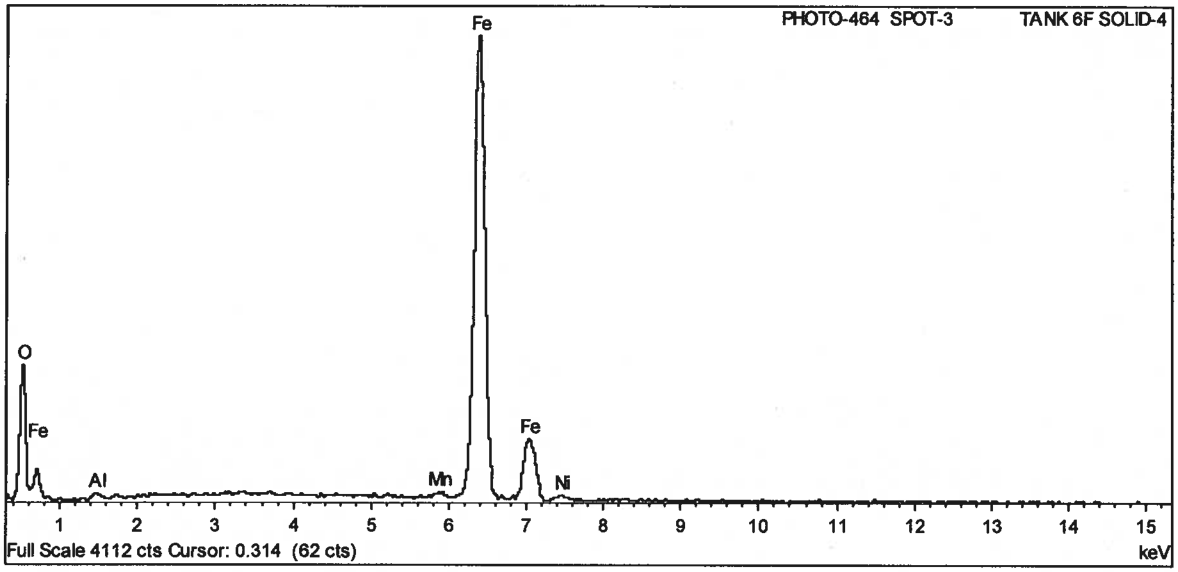

Figure 14. Tank 6F Sample 4 Spot 3

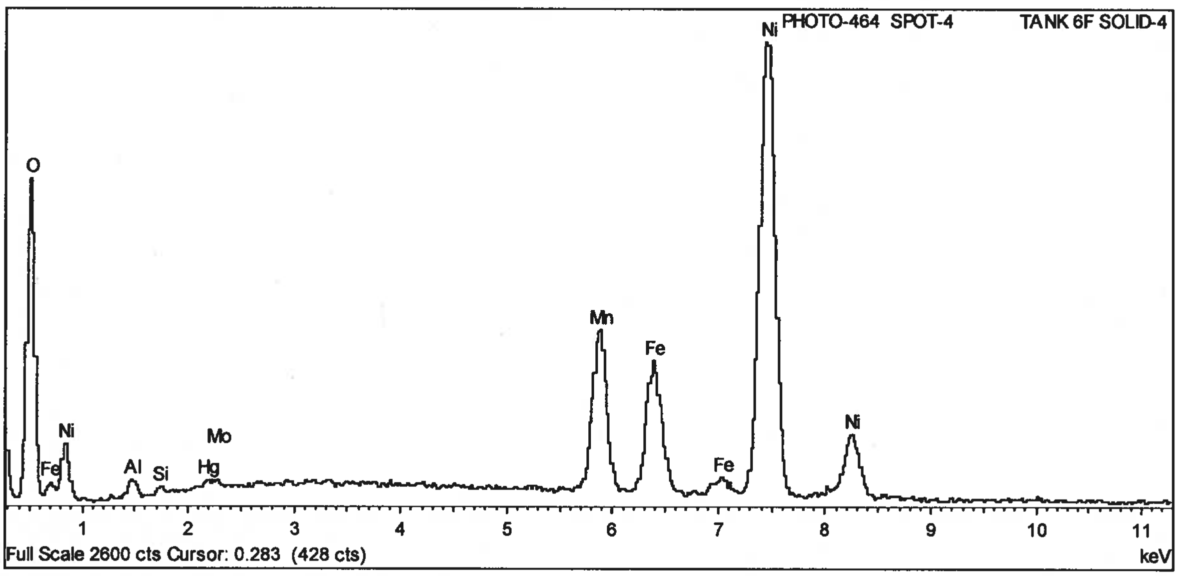

Figure 15. Tank 6F Sample 4 Spot 4

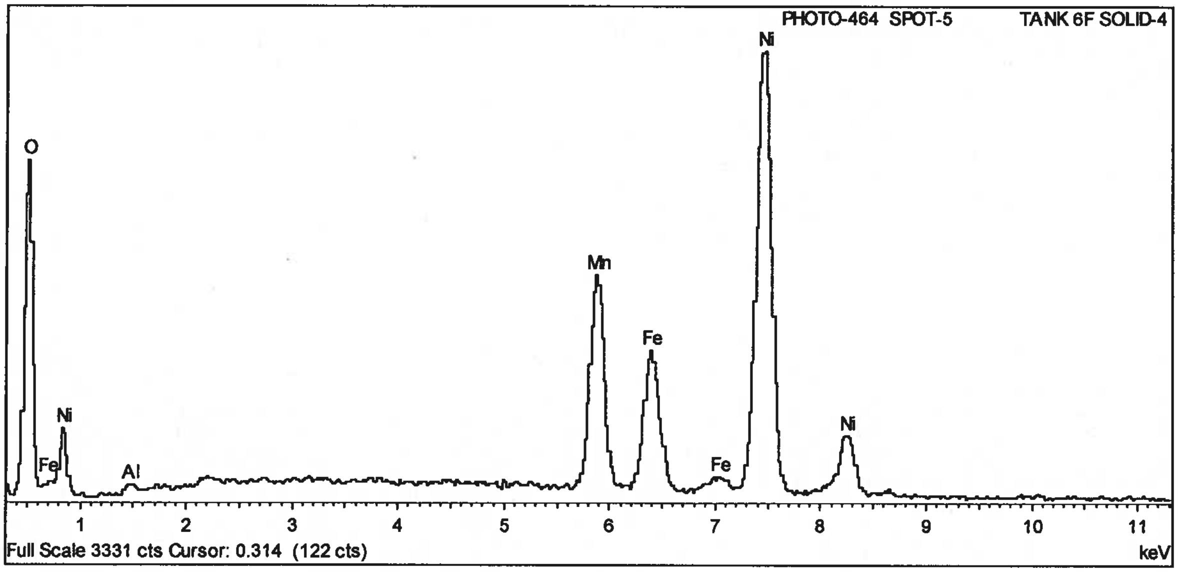

Figure 16. Tank 6F Sample 4 Spot 5

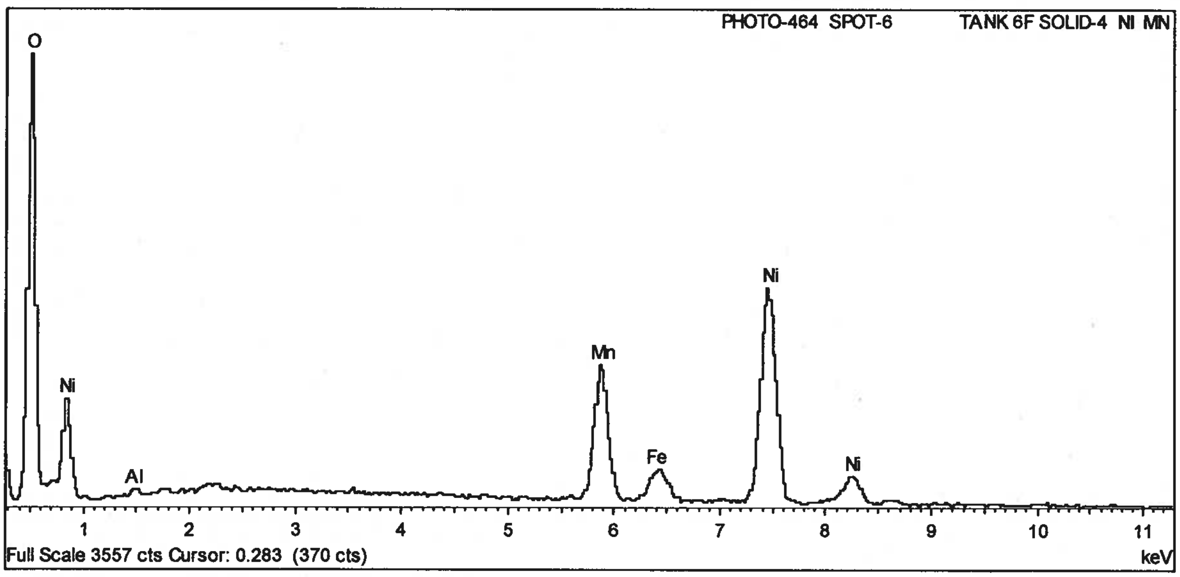

Figure 17. Tank 6F Sample 4 Spot 6

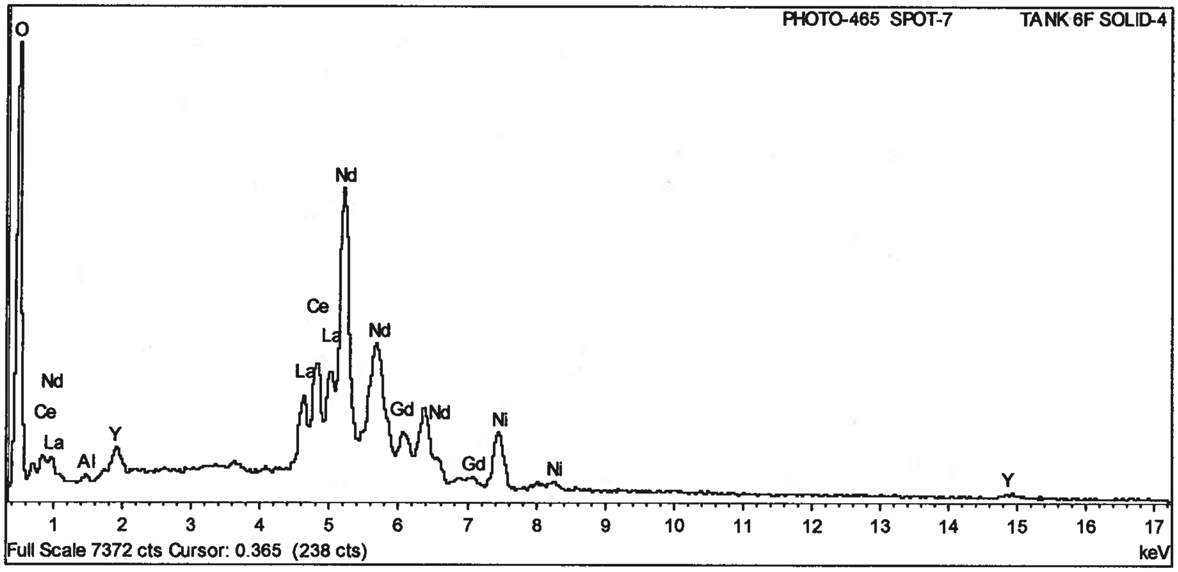

Figure 18. Tank 6F Sample 4 Spot 7

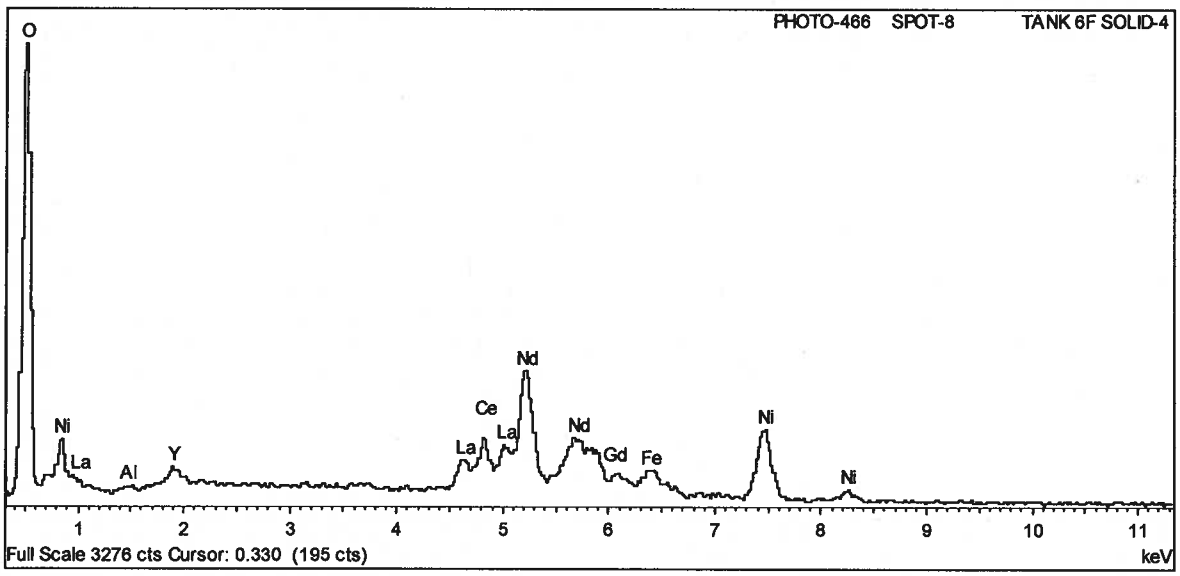

Figure 19. Tank 6F Sample 4 Spot 8

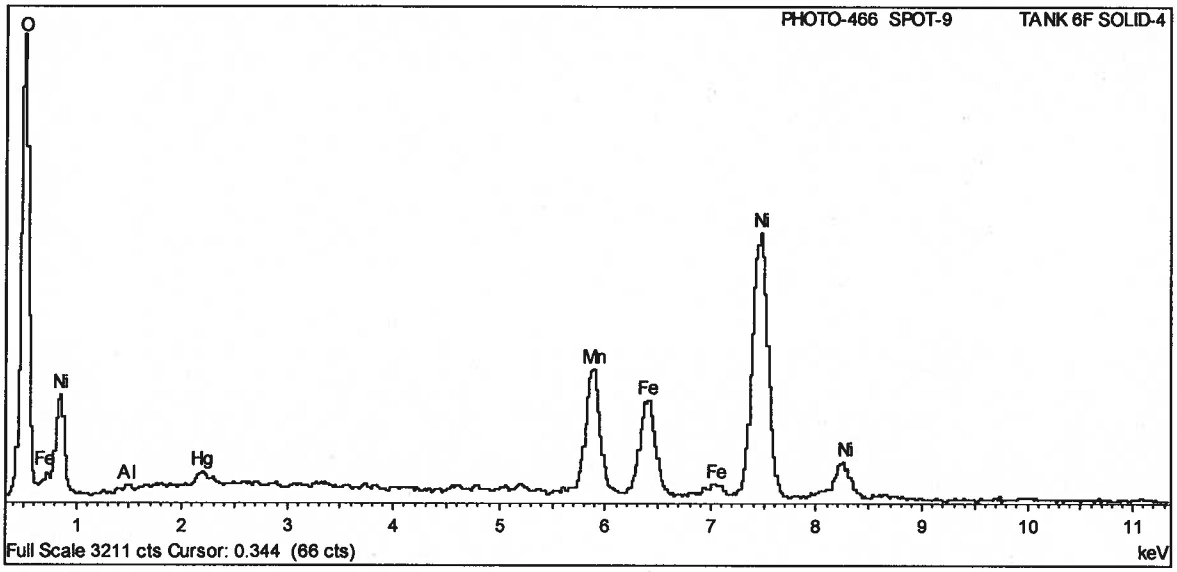

Figure 20. Tank 6F Sample 4 Spot 9

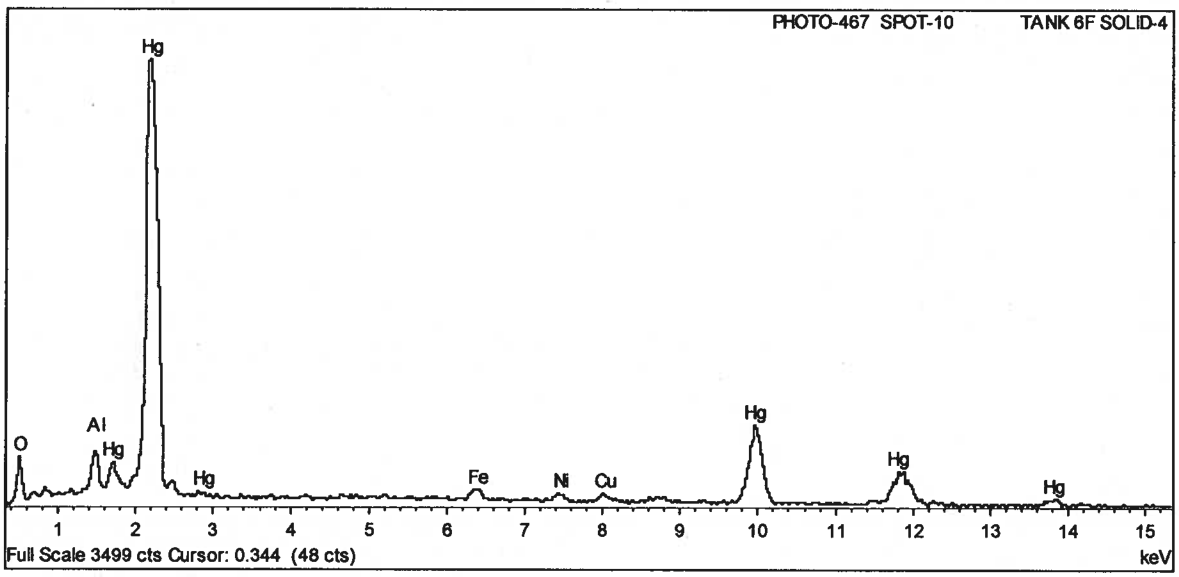

Figure 21. Tank 6F Sample 4 Spot 10

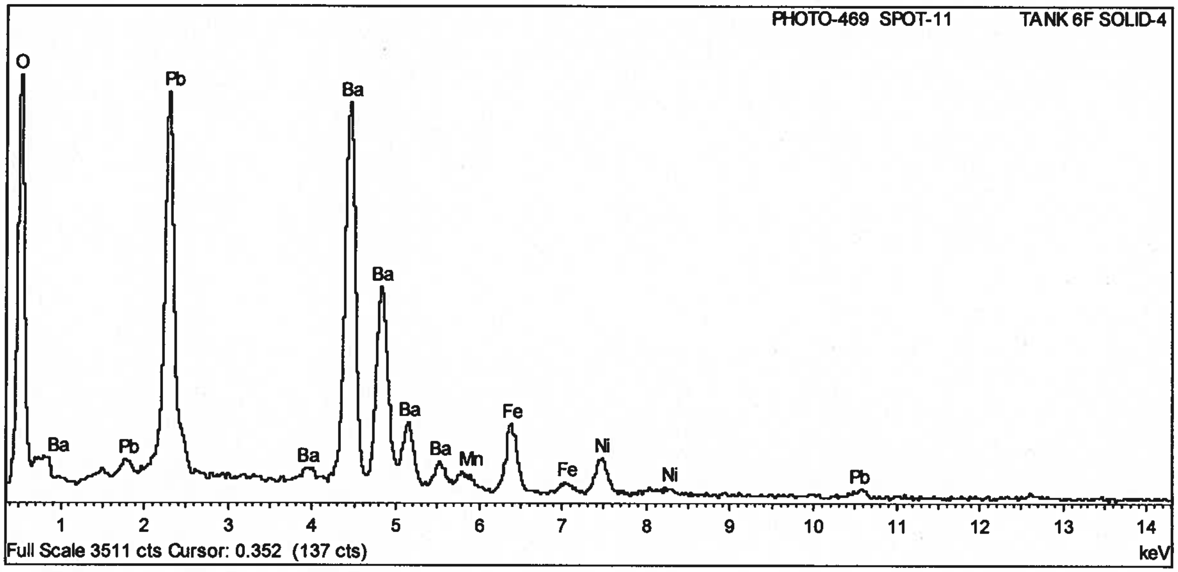

Figure 22. Tank 6F Sample 4 Spot 11

Tank 6F Sample 5

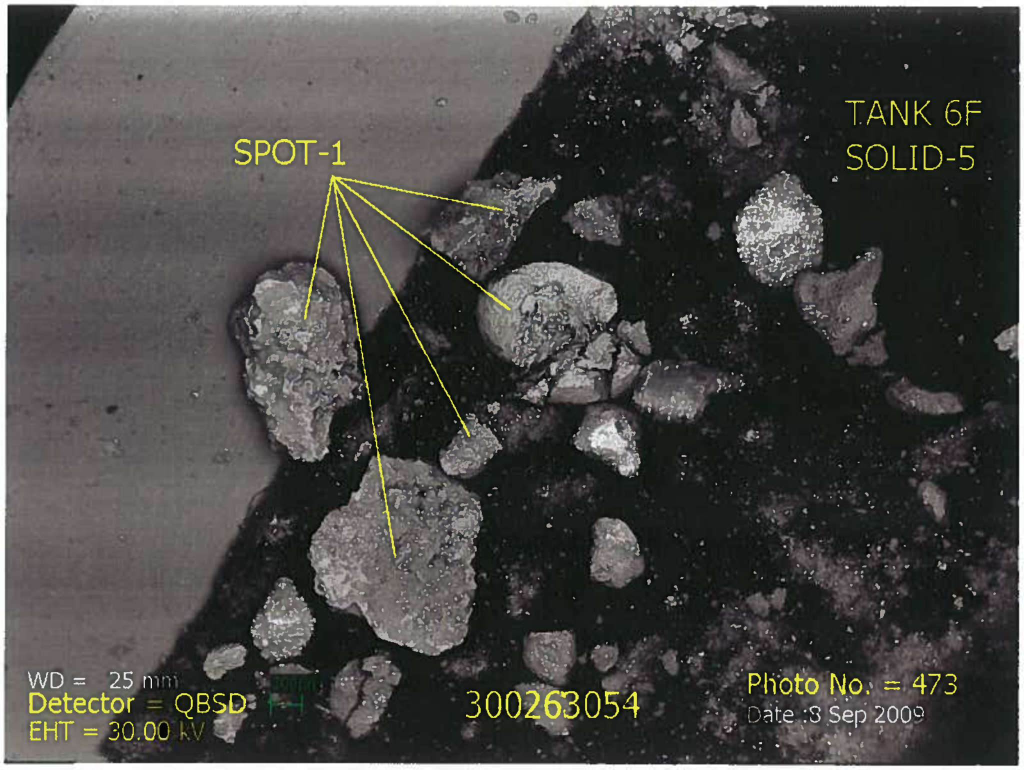

Figure 23. Tank 6F Sample 5 Spot 1

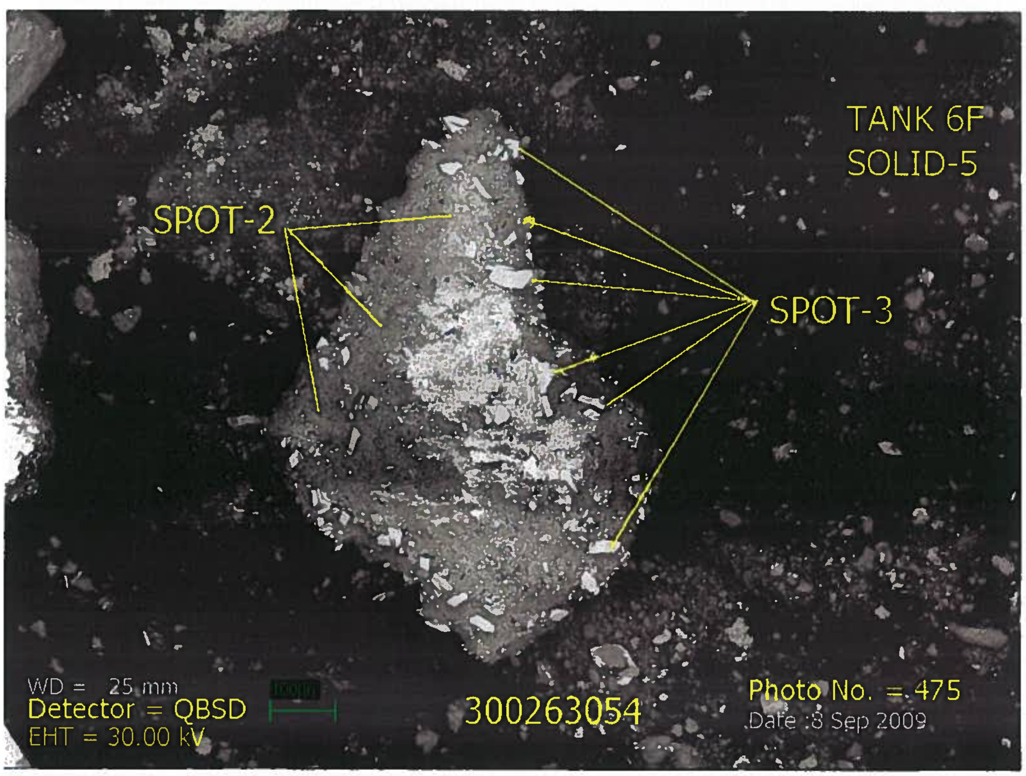

Figure 24. Tank 6F Sample 5 Spots 2 and 3

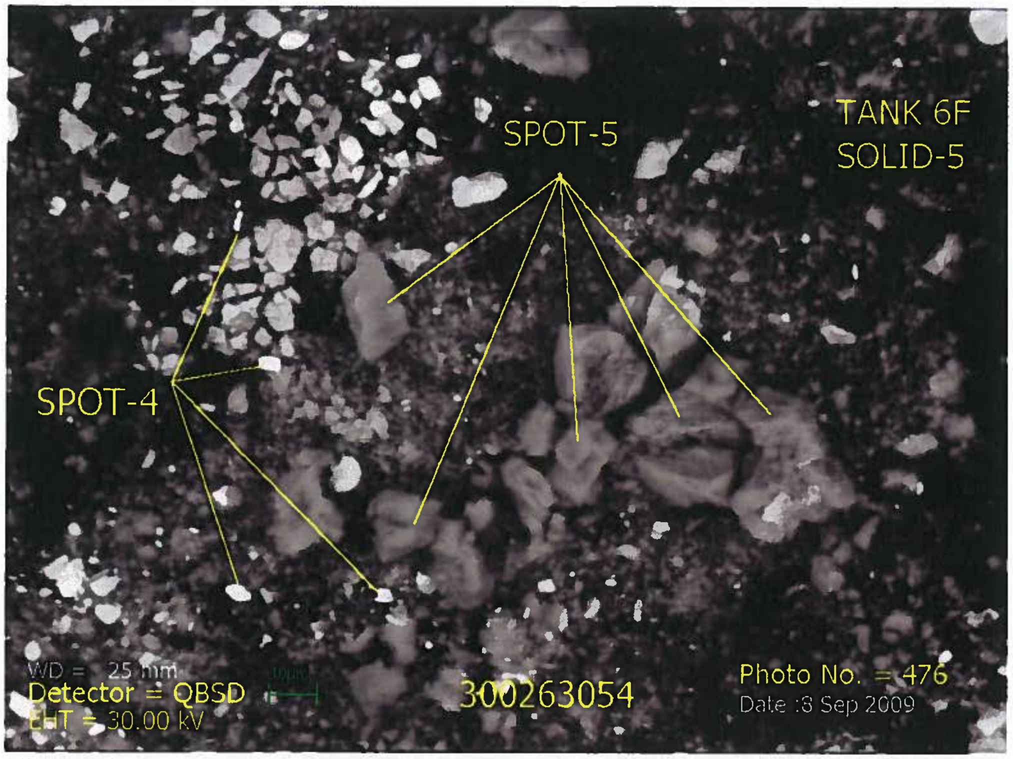

Figure 25. Tank 6F Sample 5 Spots 4 and 5

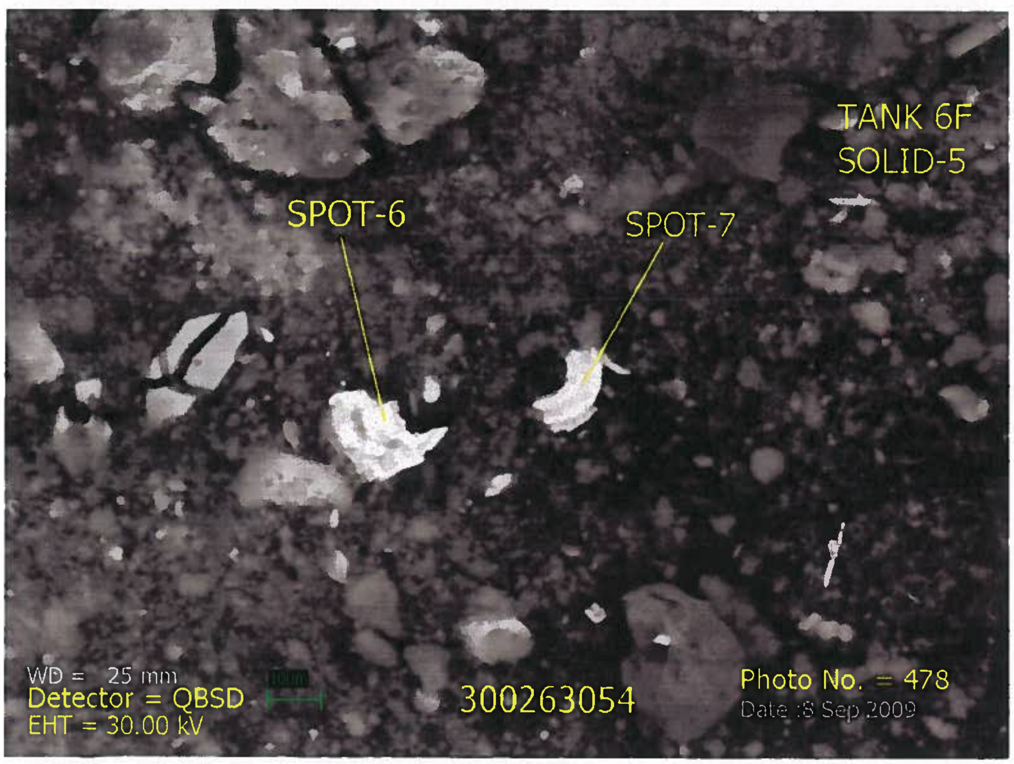

Figure 26. Tank 6F Sample 5 Spots 6 and 7

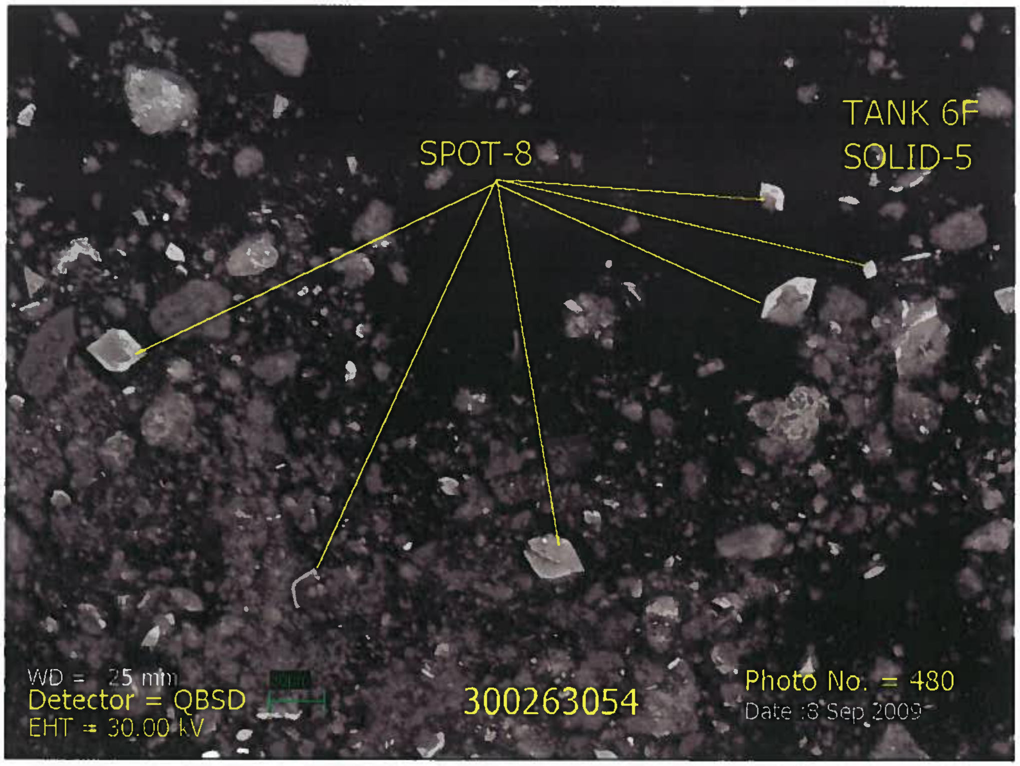

Figure 27. Tank 6F Sample 5 Spot 8

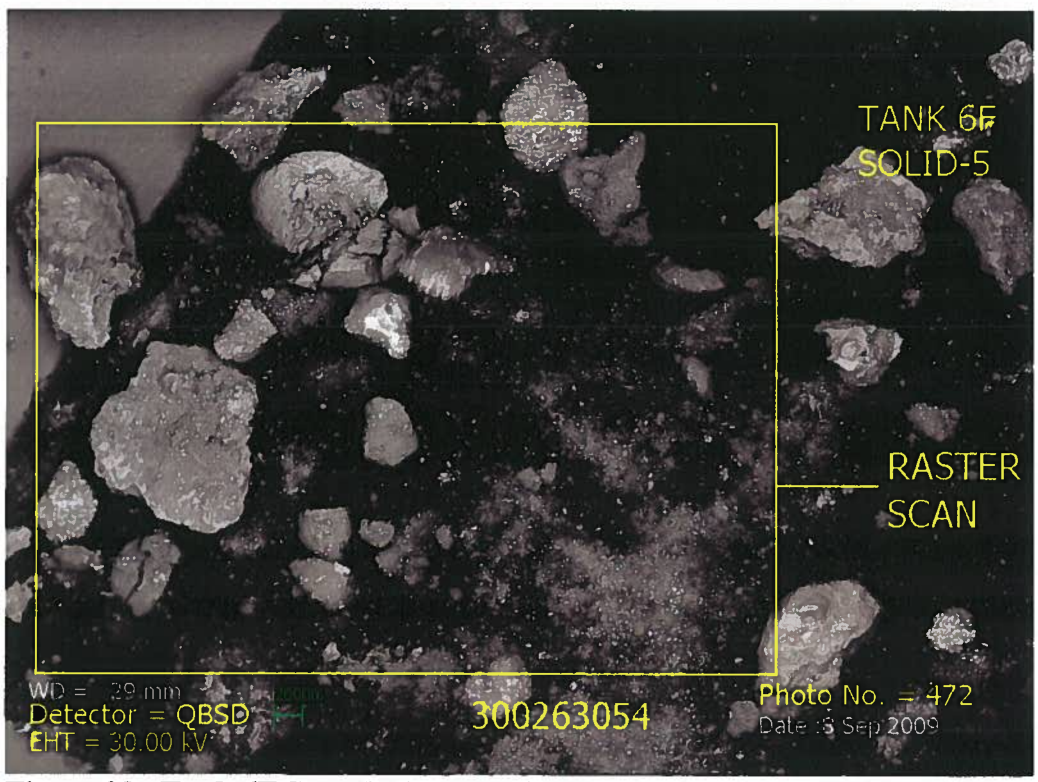

Figure 28. Tank 6F Sample 5 Raster Scan

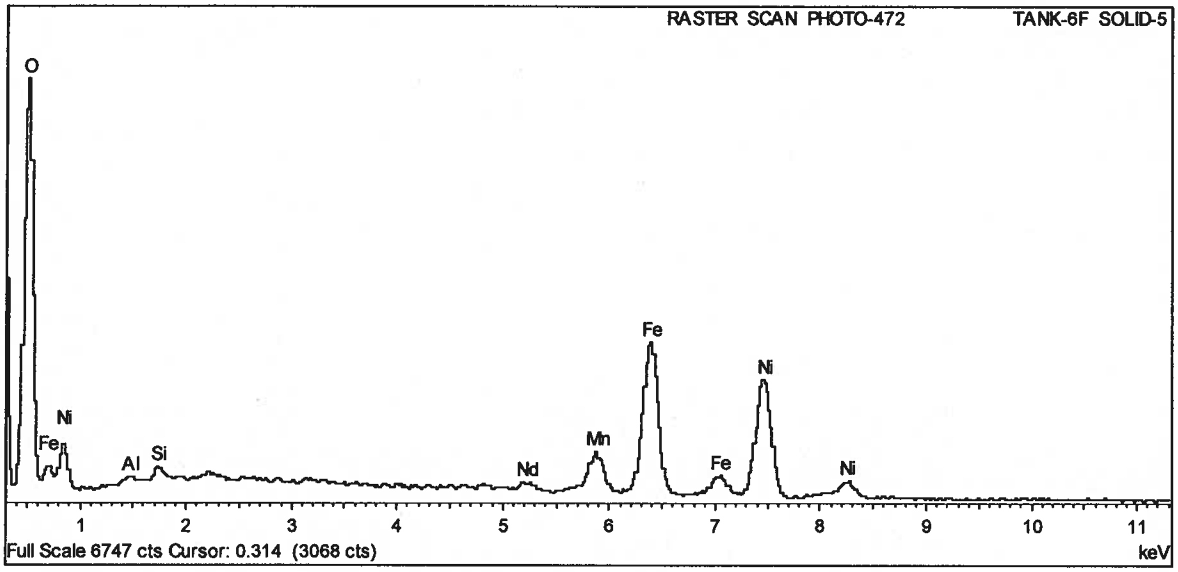

Figure 29. Tank 6F Sample 5 Raster Scan

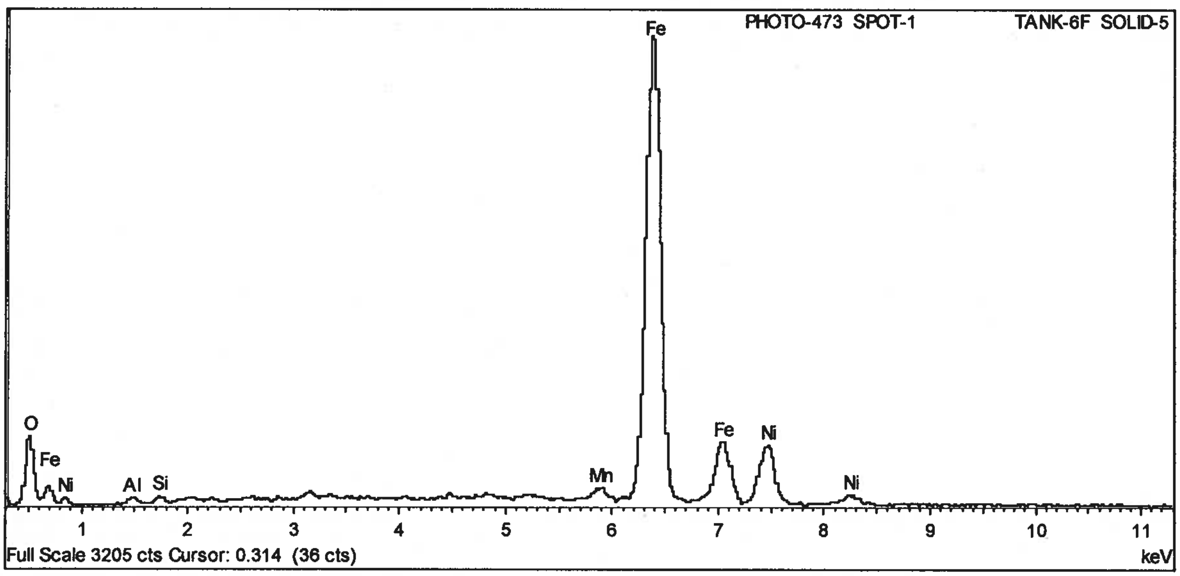

Figure 30. Tank 6F Sample 5 Spot 1

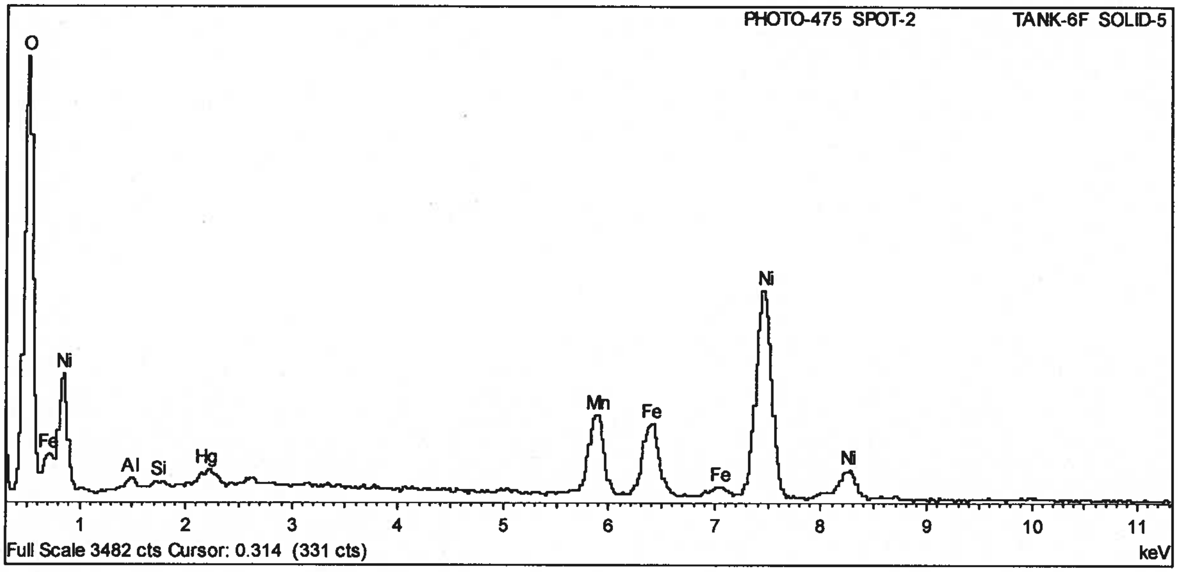

Figure 31. Tank 6F Sample 5 Spot 2

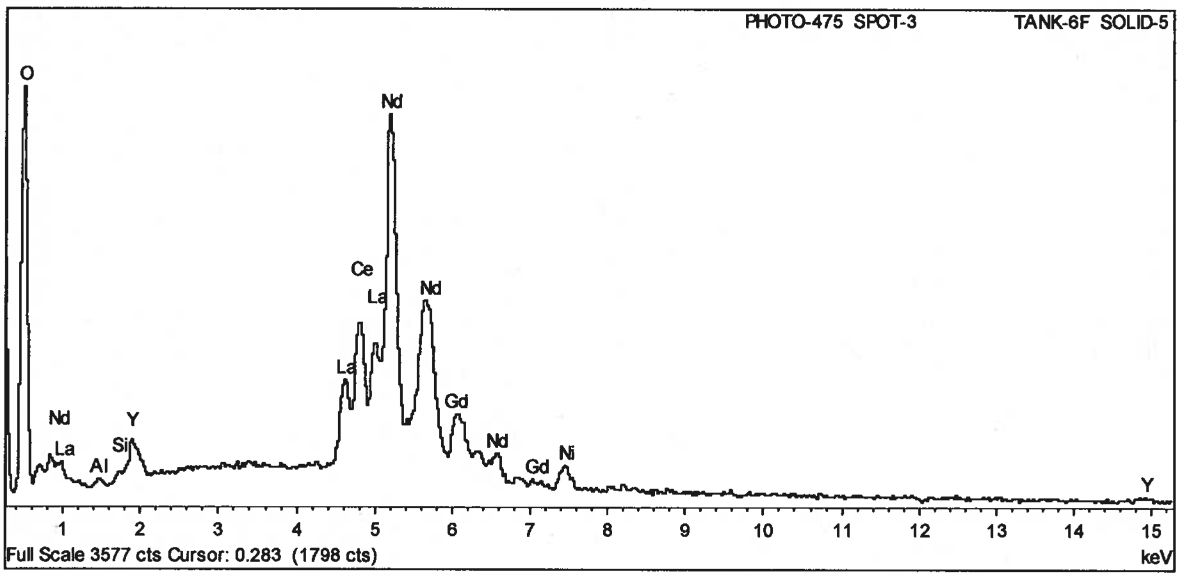

Figure 32. Tank 6F Sample 5 Spot 3

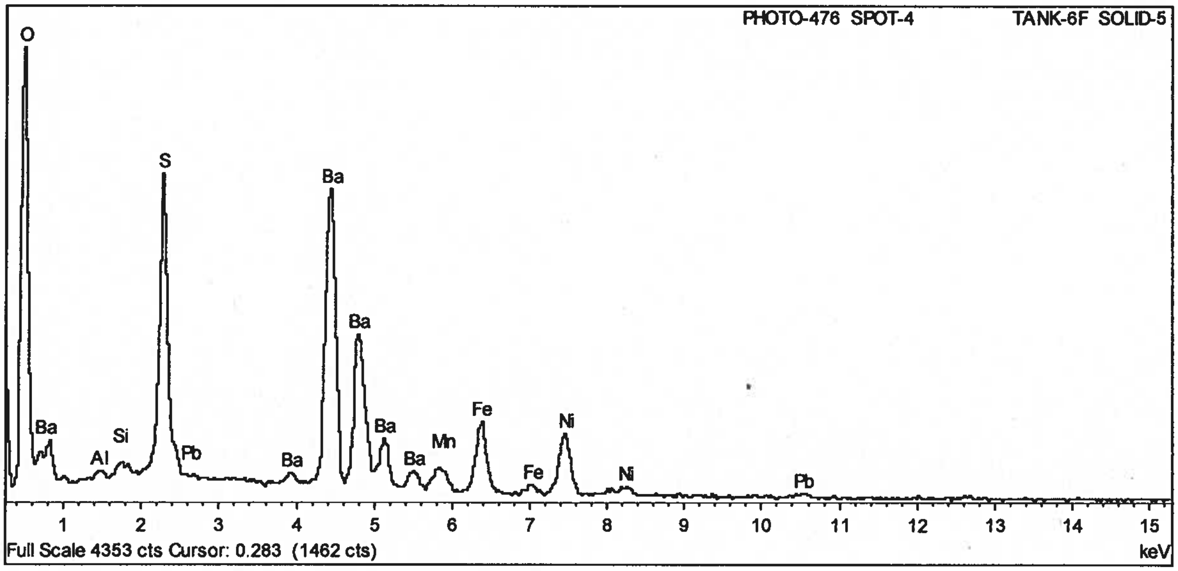

Figure 33. Tank 6F Sample 5 Spot 4

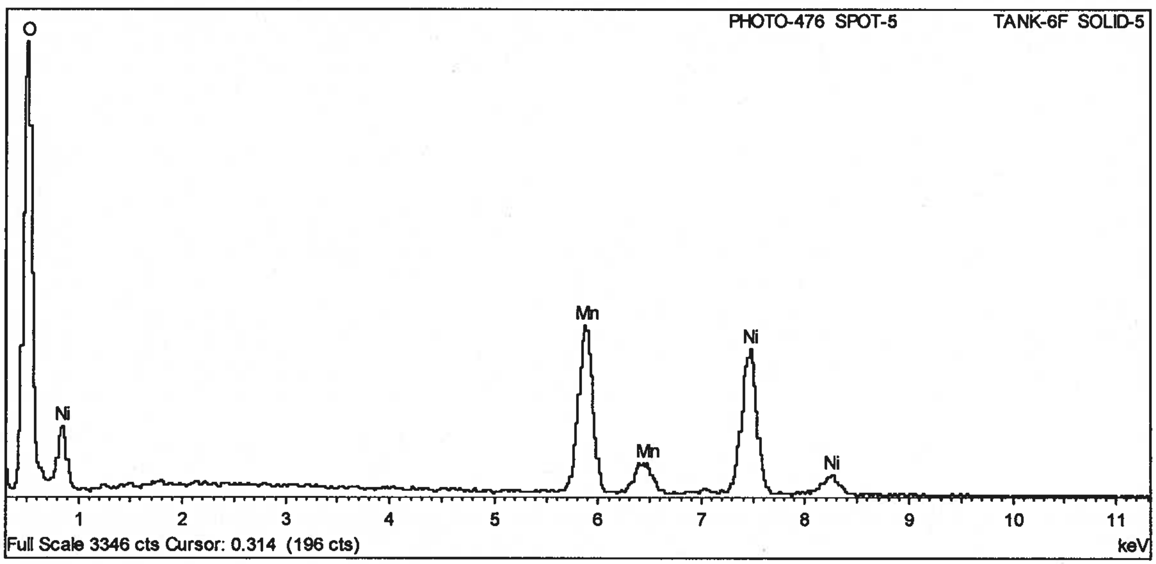

Figure 34. Tank 6F Sample 5 Spot 5

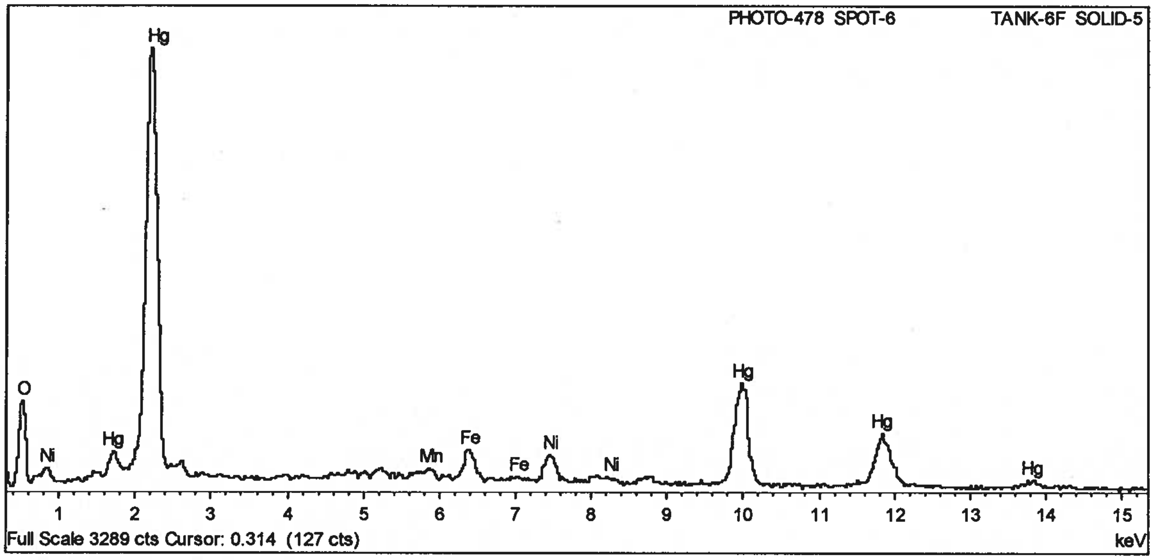

Figure 35. Tank 6 Sample 5 Spot 6

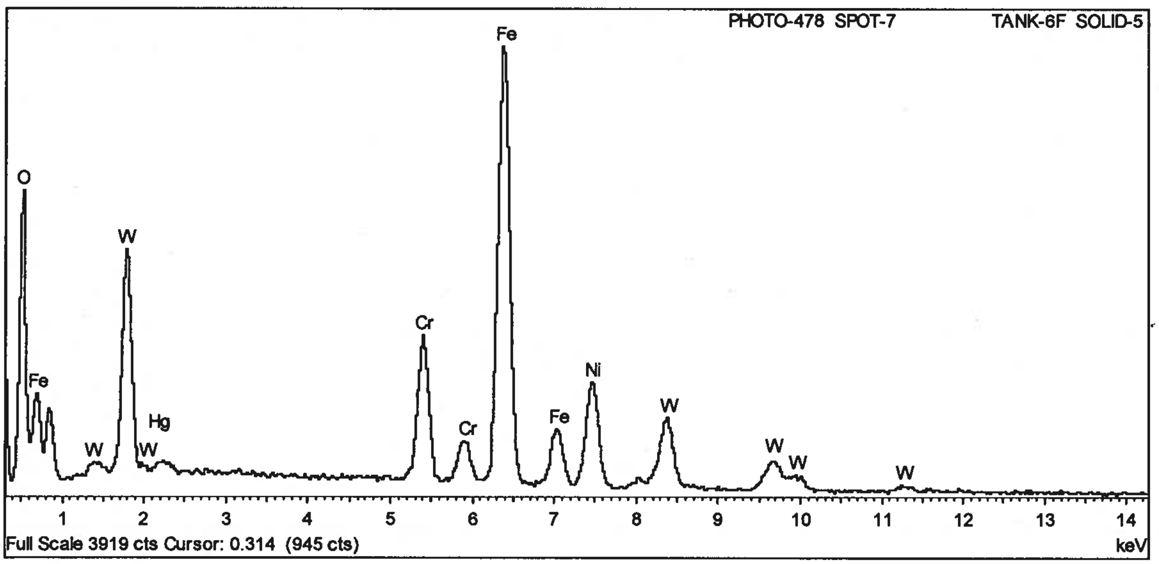

Figure 36. Tank 6F Sample 5 Spot 7

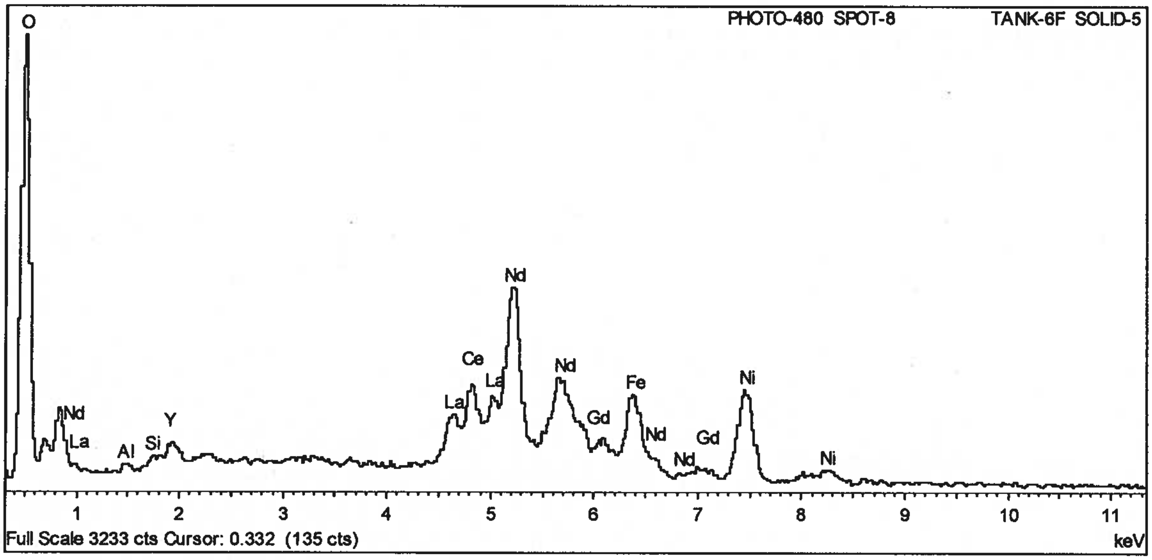

Figure 37. Tank 6F Sample 5 Spot 8

Tank 6F Sample 6

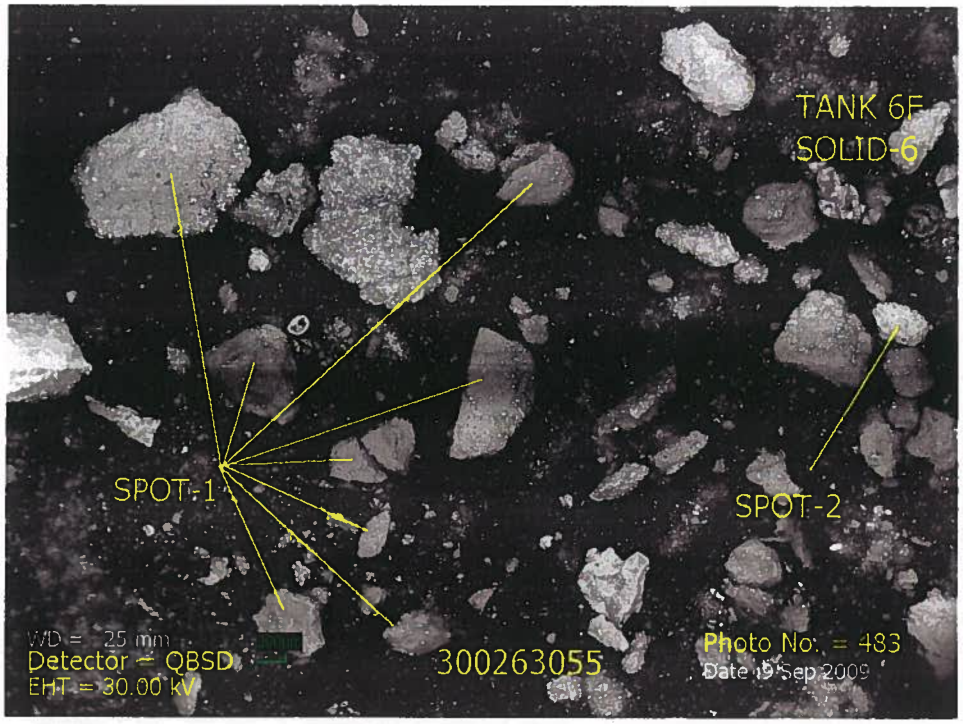

Figure 38. Tank 6F Sample 6 Spots 1 and 2

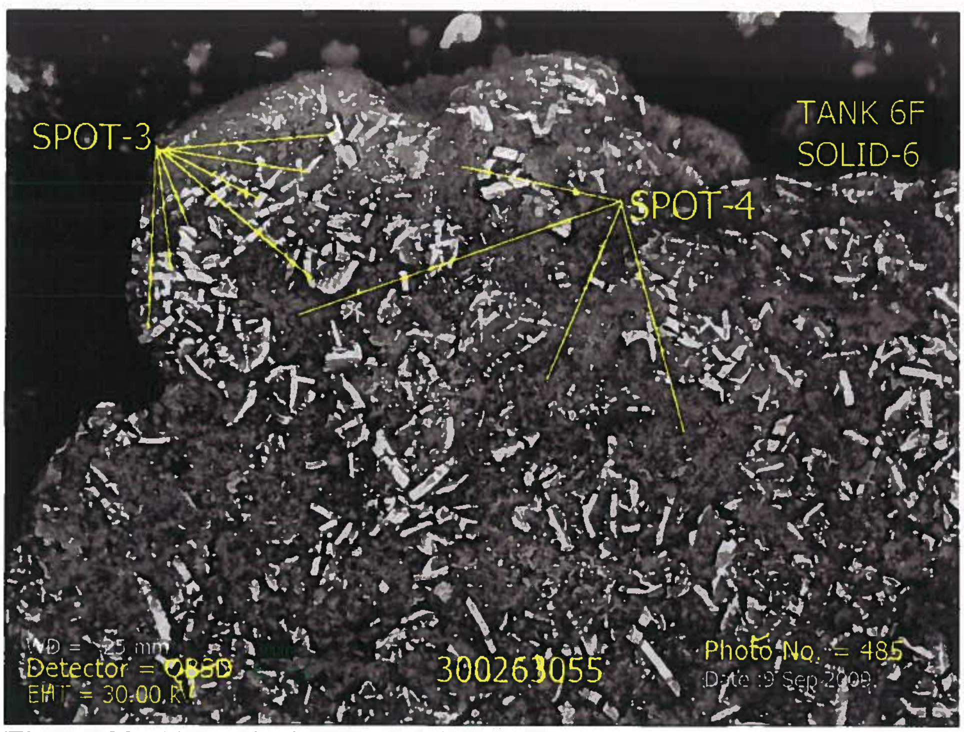

Figure 39. Tank 6F Sample 6 Spots 3 and 4

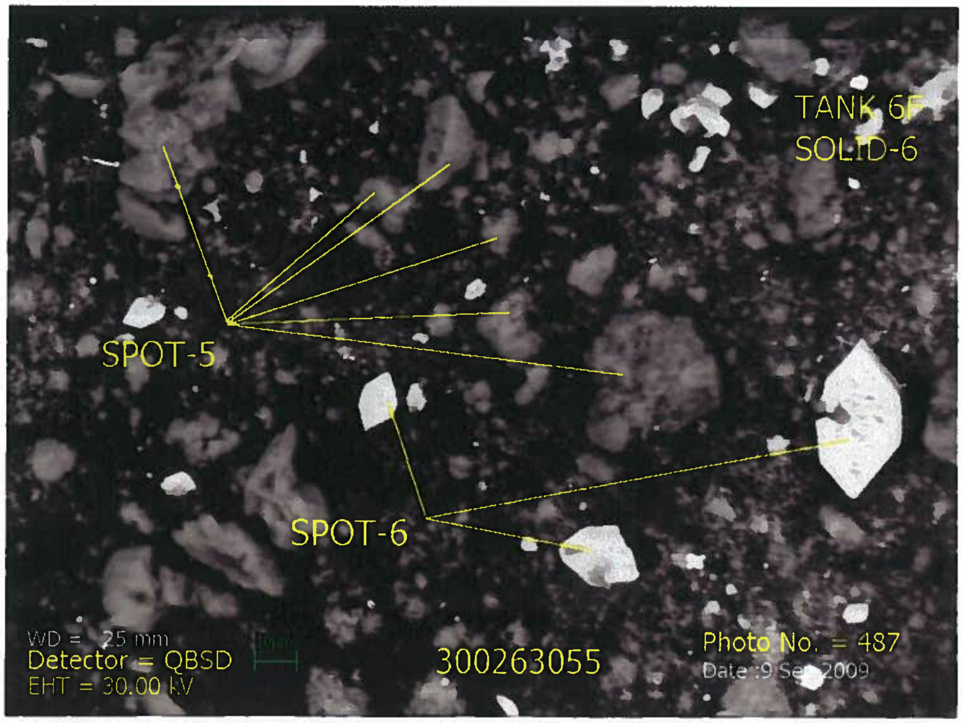

Figure 40. Tank 6F Sample 6 Spots 5 and 6

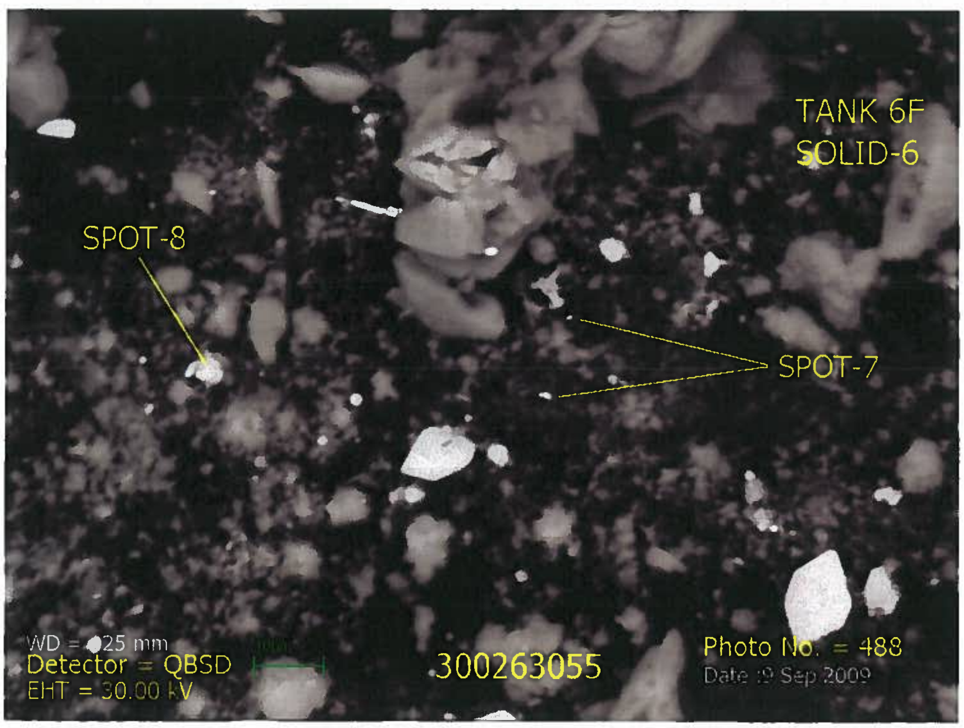

Figure 41. Tank 6F Sample 6 Spots 7 and 8

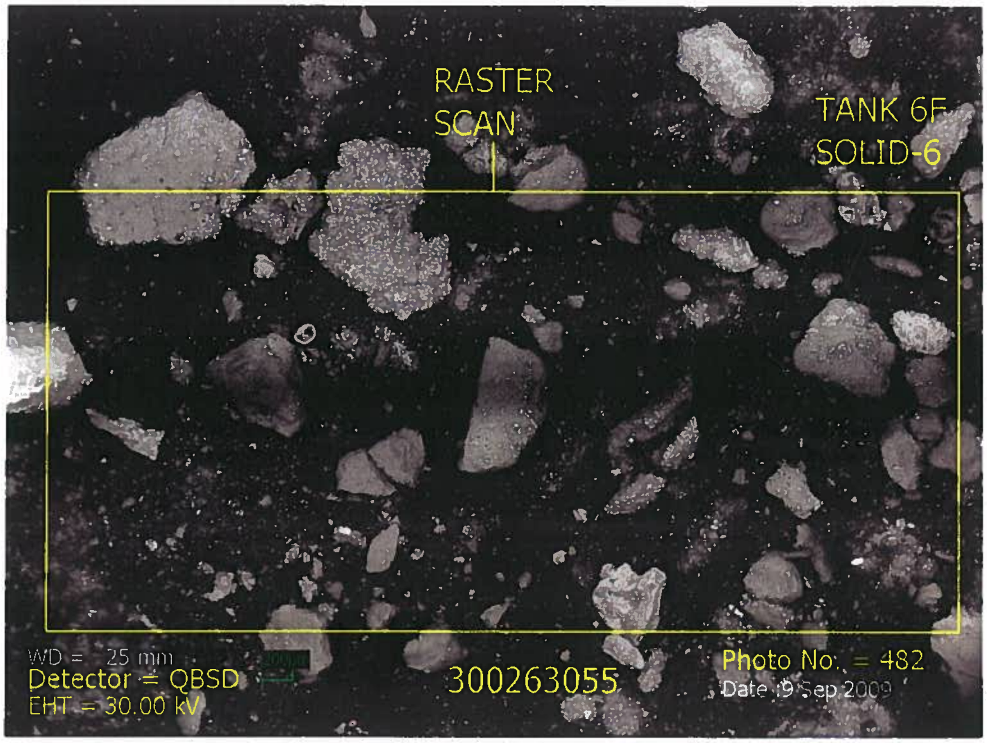

Figure 42. Tank 6F Sample 6 Raster Scan

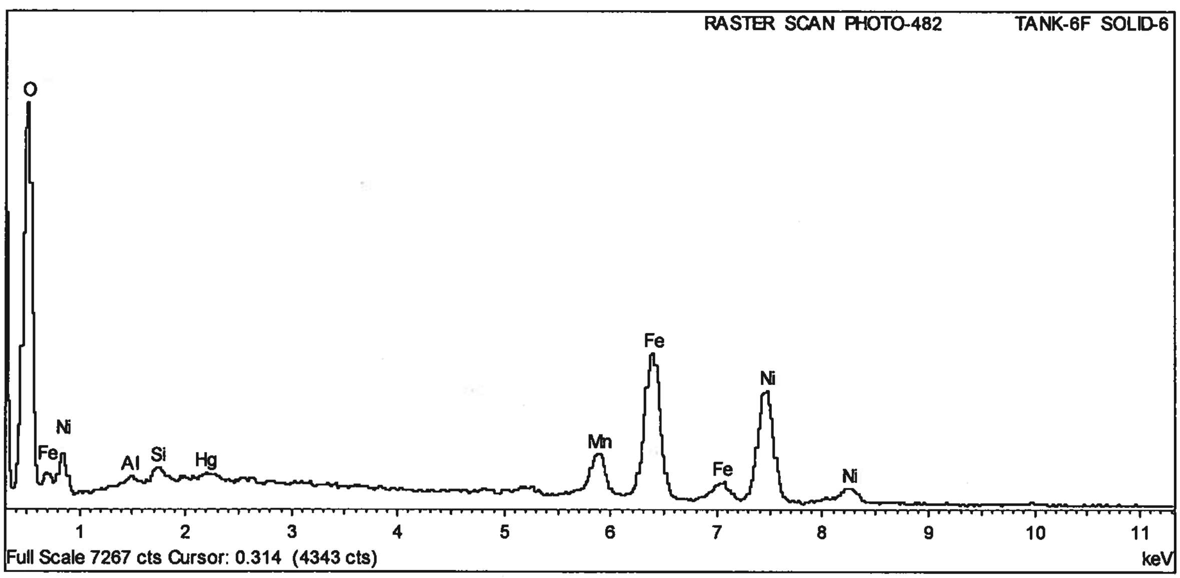

Figure 43. Tank 6F Sample 6 Raster Scan

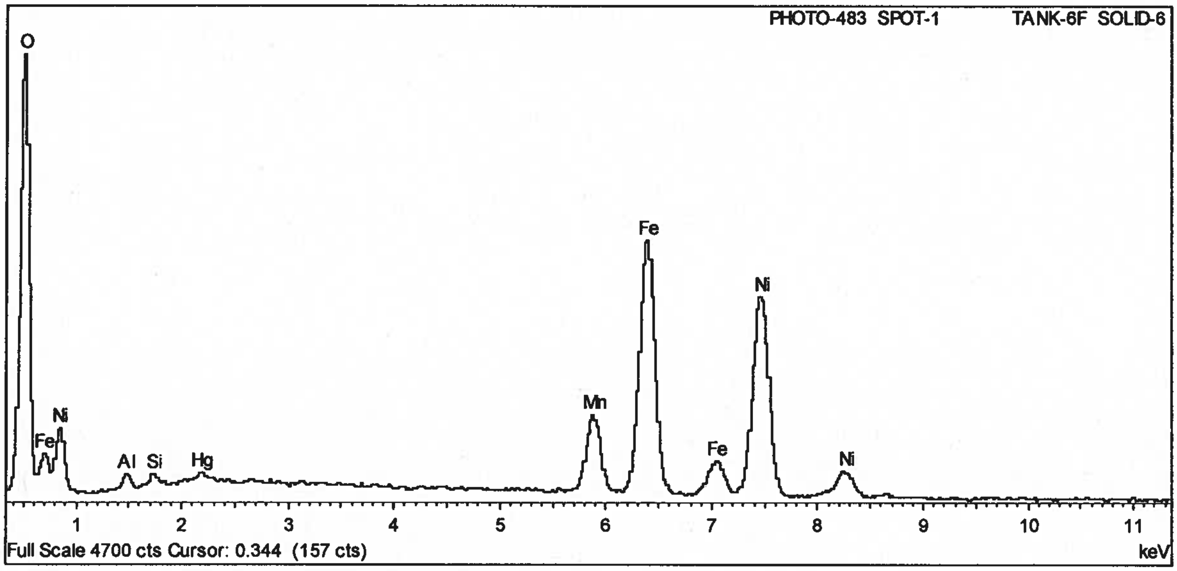

Figure 44. Tank 6F Sample 6 Spot 1

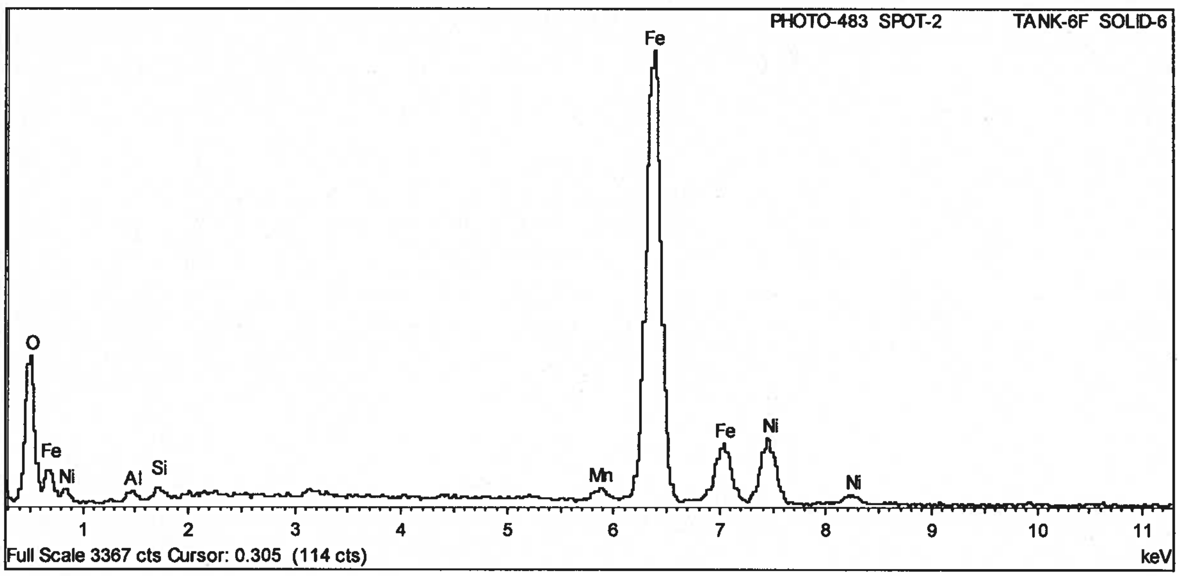

Figure 45. Tank 6F Sample 6 Spot 2

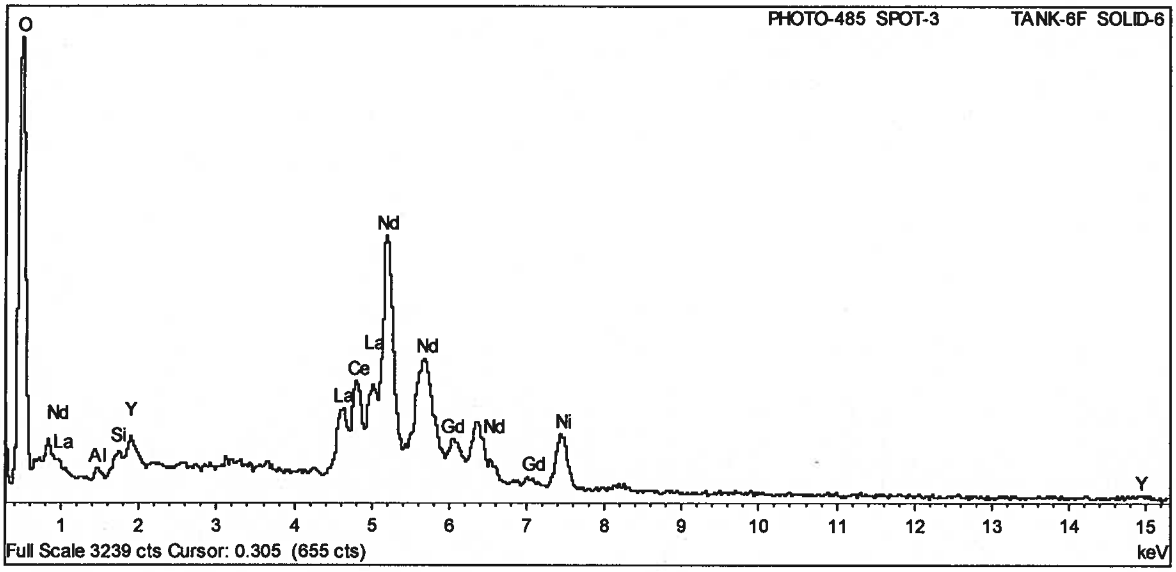

Figure 46. Tank 6F Sample 6 Spot 3

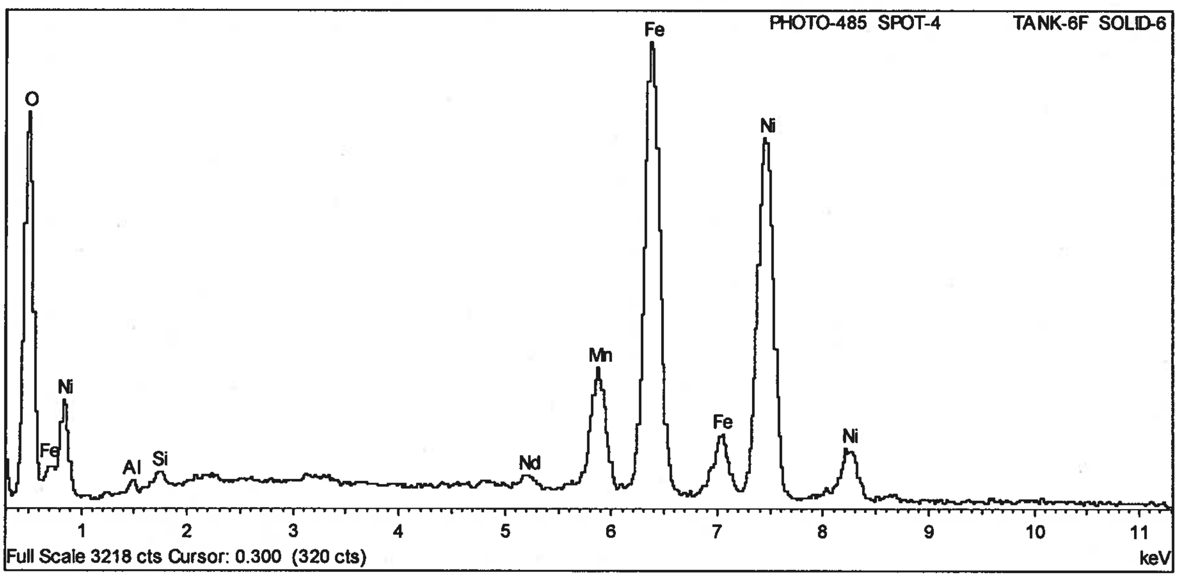

Figure 47. Tank 6F Sample 6 Spot 4

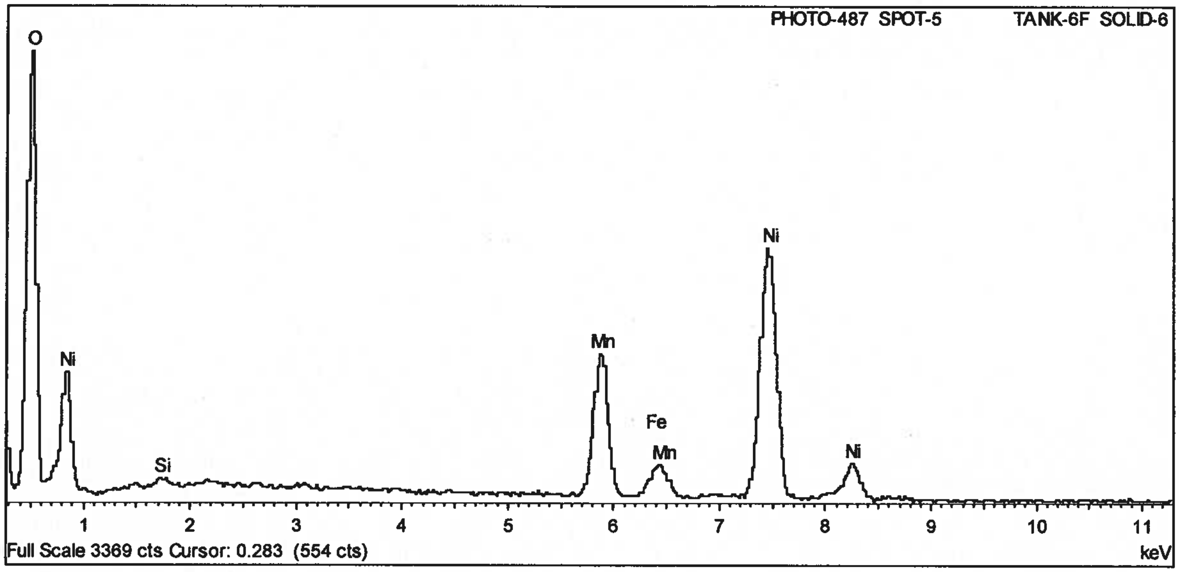

Figure 48. Tank 6F Sample 6 Spot 5

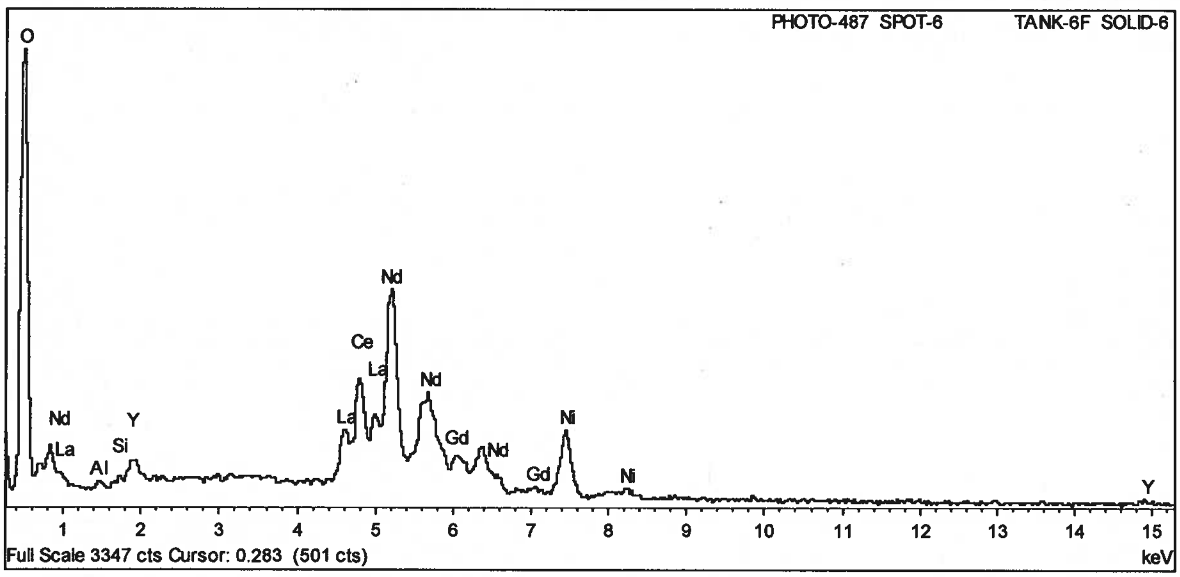

Figure 49. Tank 6F Sample 6 Spot 6

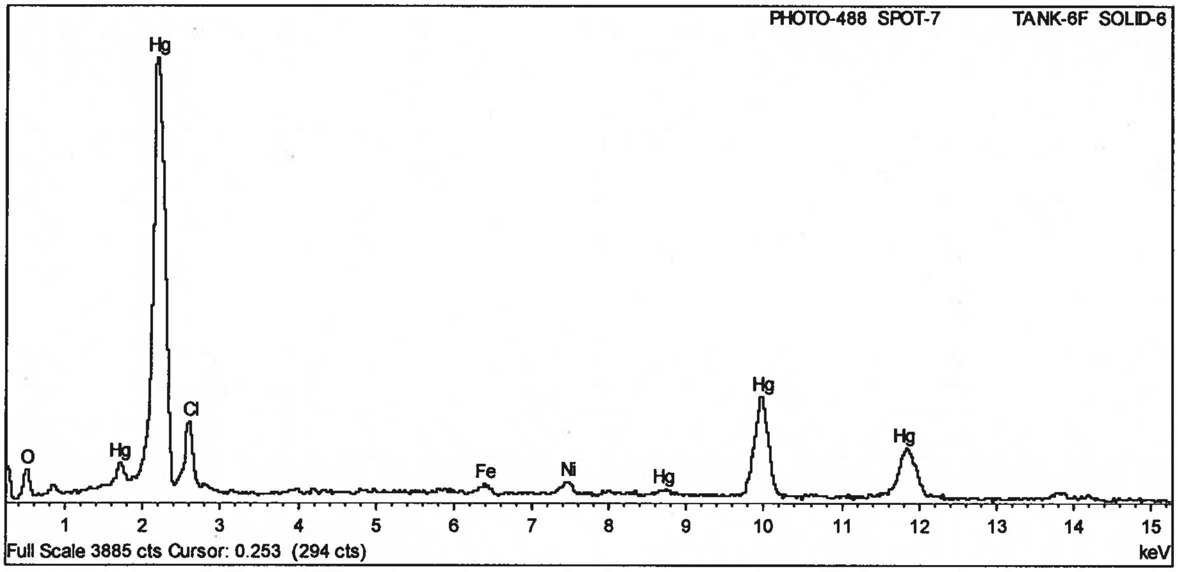

Figure 50. Tank 6F Sample 6 Spot 7

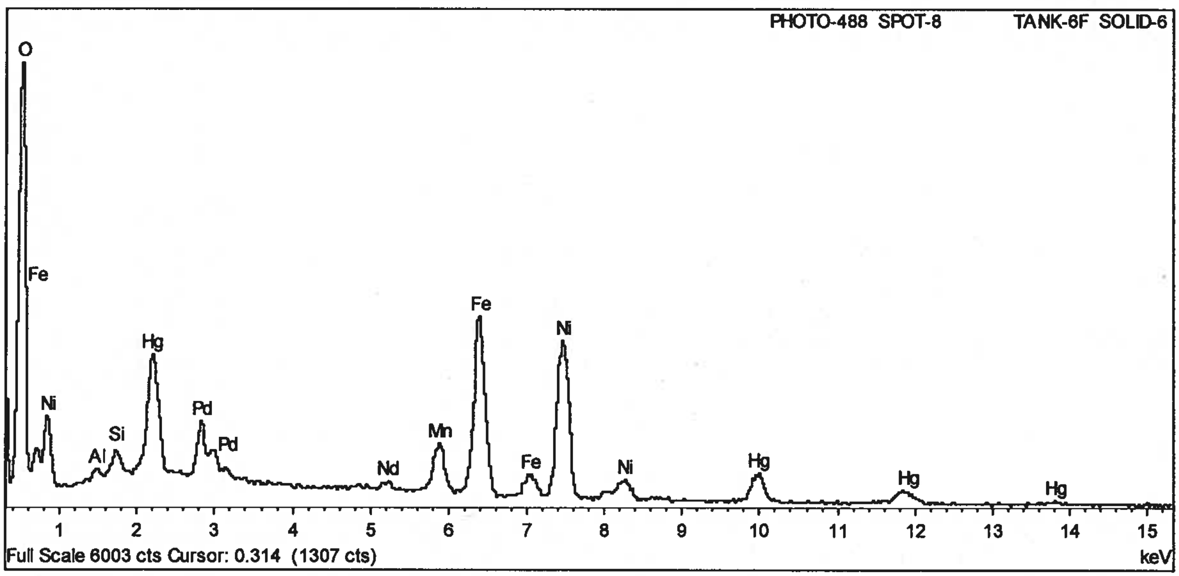

Figure 51. Tank 6F Sample 6 Spot 8

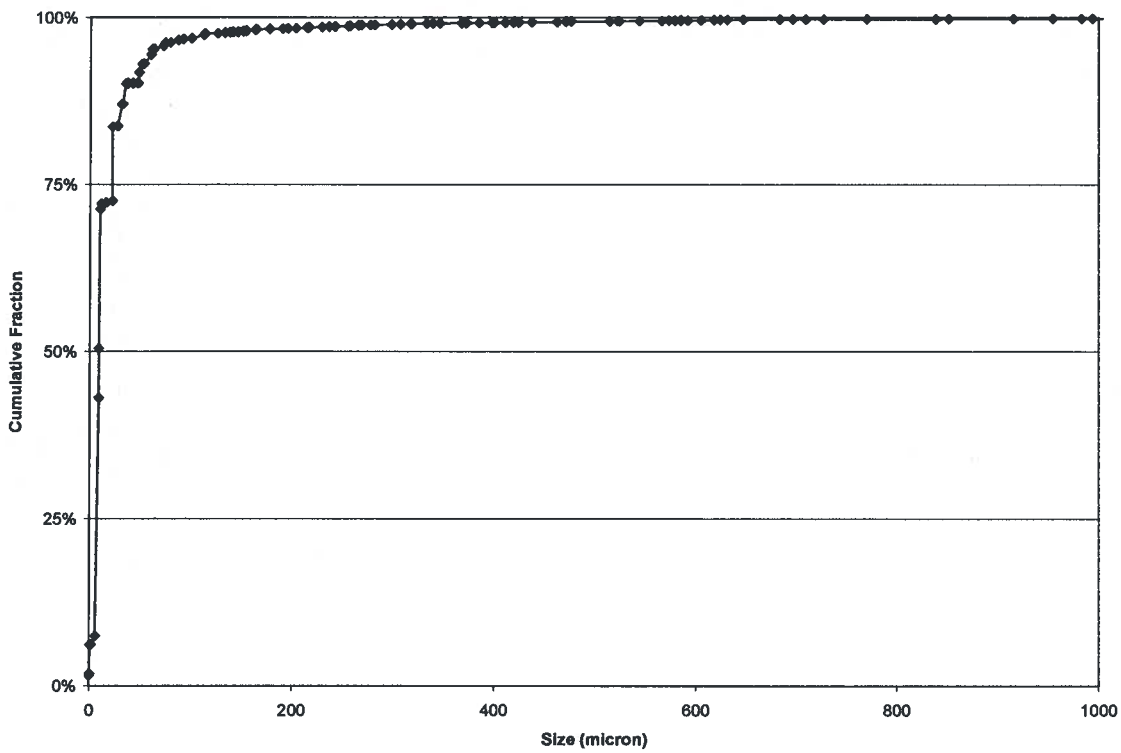

Figure 52. Tank 6F Particle Size (Number Fraction)

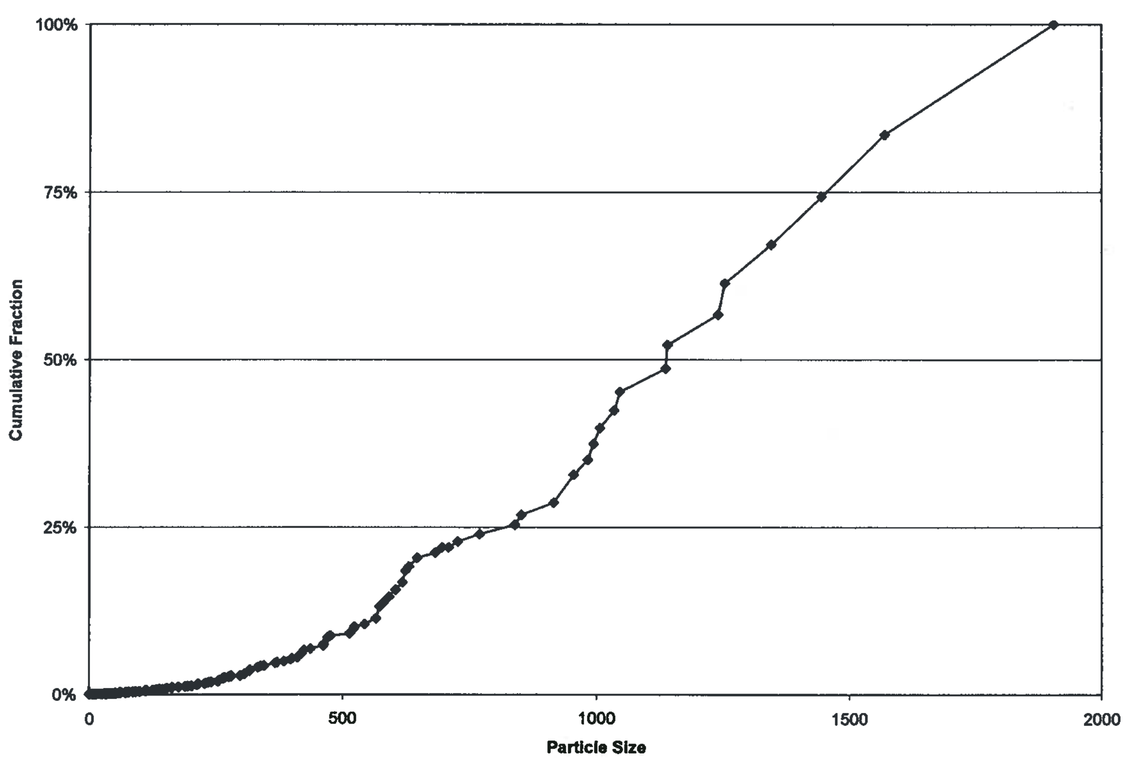

Figure 53. Tank 6F Particle Size (Volume Fraction)

5.0 CONCLUSIONS

The conclusions from this work follow.

- The dominant species measured by XRD (in order) are hematite, maghemite, nickel oxalate hydrate, and goethite.
- Hematite and nickel oxalate hydrate are not easily dissolved by oxalic acid.
- The nickel oxalate spectra measured could include contributions from manganese oxalate or ferrous oxalate.
- The primary elements identified by the SEM analysis are iron, nickel, and oxygen.
- The particle size analysis showed the highest concentration of particles between 4 and 10 microns, but some particles were as large as 2,000 microns.

When combined with the chemical analysis of the Tank 6F sample, this data suggests that additional acid strikes are unlikely to remove a significant fraction of the remaining sludge mass.

6.0 REFERENCES

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