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Preparation and Initial Characterization of Fluidized Bed Steam Reforming Pure-Phase Standards

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EXECUTIVE SUMMARY

Hanford is investigating the Fluidized Bed Steam Reforming (FBSR) process for their Low Activity Waste. The FBSR process offers a low-temperature continuous method by which liquid waste can be processed with the addition of clay into a sodium aluminosilicate (NAS) waste form. The NAS waste form is mainly comprised of nepheline ($NaAlSiO_4$), sodalite ($Na_8[AlSiO_4]_6Cl_2$), and nosean ($Na_8[AlSiO_4]_6SO_4$). Anions such as perrhenate (ReO_4^-), pertechnetate (TcO_4^-), and iodine (I^-) are expected to replace sulfate in the nosean structure and/or chloride in the sodalite mineral structure (atomically bonded inside the aluminosilicate cages that these mineral structures possess).

In the FBSR waste form, each of these phases can exist in a variety of solid solutions that differ from the idealized forms observed in single crystals in nature. The lack of understanding of the durability of these stoichiometric or idealized mineral phases complicates the ability to deconvolute the durability of the mixed phase FBSR product since it is a combination of different NAS phases. To better understand the behavior, fabrication and testing of the individual phases of the FBSR product is required.

Analytical Development (AD) of the Science and Technology directorate of the Savannah River National Laboratory (SRNL) was requested to prepare the series of phase-pure standards, consisting of nepheline, nosean, and Cl, Re, and I sodalite. Once prepared, X-ray Diffraction (XRD) analyses were used to confirm the products were phase pure. These standards are being used for subsequent characterization studies consisting of the following: single-pass flow-through (SPFT) testing, development of thermodynamic data, and x-ray diffraction (XRD) calibration curves. In addition to the above mentioned phase-pure standards, AD was tasked with fabricating a mixed Tc-Re sodalite.

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LIST OF ABBREVIATIONS

AD	Analytical Development
ASAP	Accelerated Surface Area and Pore Analyzer
BET	Brunauer-Emmitt-Teller
DPT	Differential Pressure Transducer
FBSR	Fluidized Bed Steam Reforming
ICDD	International Centre for Diffraction Data
JCPDS	Joint Committee on Powder Diffraction Standards
LAW	Low Activity Waste
NAS	Sodium Aluminosilicate
ORNL	Oak Ridge National Laboratory
PSD	Particle Size Distribution
PDF	Powder Diffraction File
RS	Receiving Slit
SEM-EDS	Scanning Electron Microscopy – Energy Dispersive X-ray Spectrometer
SPFT	Single Pass Flow Through Test
SRNL	Savannah River National Laboratory
SS	Soller Slit
SW	Secondary Waste
TTT	THOR® Treatment Technologies
UCD	University of California - Davis
WTP	Waste Treatment Plant
XRD	X-ray Diffraction
ZTIT	zeolite thermally induced transformation

1.0 Introduction

Hanford is investigating the use of Fluidized Bed Steam Reforming (FBSR) as a Supplemental Treatment technology for their Low Activity Waste (LAW). THOR® Treatment Technologies (TTT) has successfully demonstrated the FBSR technology at the pilot scale using a Hanford Waste Treatment Plant-Secondary Waste (WTP-SW) non-radioactive simulant[1] and a Hanford 69 tank blend known as the Rassat simulant[2]. However, additional data on actual radioactive Hanford tank waste as well as actual performance data is required to further evaluate the technology for the down select of the Supplemental Treatment technology.

The Savannah River National Laboratory has been tasked with performing Bench-Scale Steam Reforming (BSR) with simulant and radioactive waste samples bounding the potential Hanford LAW streams using the FBSR technology with the addition of clay minerals to produce sodium aluminosilicate (NAS) waste forms[3,4]. The NAS waste form is mainly comprised of nepheline ($NaAlSiO_4$), sodalite ($Na_8[AlSiO_4]_6Cl_2$), and nosean ($Na_8[AlSiO_4]_6SO_4$). Anions such as perrhenate (ReO_4^-), pertechnetate (TcO_4^-), are expected to replace sulfate in the nosean structure and iodine (I^-) is expected to replace chloride the sodalite mineral structure (atomically bonded inside the aluminosilicate cages that these mineral structures possess).

In the FBSR waste form, each of these phases can exist in a variety of solid solutions that differ from the idealized forms observed in single crystals in nature. The lack of understanding of the durability of these stoichiometric or idealized mineral phases complicates the ability to deconvolute the durability of the mixed phase FBSR product since it is a combination of different NAS phases. To gain understanding on the durability of these primary mineral phases in the FBSR product, pure-phase standards were fabricated by solid-state, modified solid state, or hydrothermal techniques. These standards are being used to perform single-pass flow-through testing at Oak Ridge National Laboratory (ORNL), develop thermodynamic data at University of California-Davis (UCD), and develop quantitative XRD calibration curves. This document describes the different processes used to fabricate the single phase standards along with initial characterization using XRD (to determine if the material is phase-pure), particle size distribution (PSD), and Brunauer-Emmett-Teller (BET) surface area.

2.0 Experimental Procedure

2.1 Synthesis Trials

As part of the SRNL FBSR project, AD was requested to synthesize five phase-pure compounds, since none are available as a commercial product nor can they be obtained in any significant quantity as a phase-pure mineral.

Several attempts were made to synthesize nepheline using a solid-state reaction based on the Joint Committee on Powder Diffraction Standards, JCPDS, card file[5]. Table Table 2-1 below outlines the different starting materials used along with the amounts. Each of these attempts produced nepheline, but the XRD spectra always contained extra peaks making the material multiphase instead of phase-pure. In the last two attempts listed in Table 2-1 below, the starting materials were first dissolved, dried, ground, and then heated. An extra amount of the sodium aluminate was added in the last attempt since the previous attempt XRD indicated a small amount of silica that was not incorporated into the nepheline structure. In a paper by Dimitrijevic, he used the zeolite thermally induced transformation (ZTIT) route to synthesize phase-pure nepheline by converting a 4A-type zeolite[6].

Table 2-1. Initial Attempts to Synthesize Nepheline

Trial #	0.03 μm SiO_2 Moles	5 μm SiO_2 Moles	Ludox Moles	Kaolin Moles	γ Al_2O_3 Moles	$NaAlO_2$ Moles	$NaHCO_3$ Moles	Reaction Time and Temperature
1	0.021				0.010		0.021	494hrs @ 1000°C, 54hrs @ 1025°C
2		0.100			0.050		0.100	494hrs @ 1000°C, 54hrs @ 1025°C
3				0.050			0.100	494hrs @ 1000°C, 54hrs @ 1025°C
4			0.100			0.100		370hrs @ 1000°C, 218hrs @ 1025°C, 90hrs @ 1050°C, 63hrs @ 1075°C
5			0.100			0.105		24hrs @ 800°C, 370hrs @ 1000°C, 218hrs @ 1025°C, 90hrs @ 1050°C, 63hrs @ 1075°C

The initial synthesis of nosean started with a low- and a high-temperature hydrothermal method. The low-temperature synthesis was based on the NaBr-sodalite recipe from the International Zeolite Association website[7], and the high-temperature was derived from a paper by Trill, Eckert, and Srdanov[8]. Both recipes were adjusted several times and each used an excess amount of sodium sulfate and sodium hydroxide, which was subsequently washed out. A single attempt was derived from a paper by Mattigod[9]. Table 2-2 outlines the different starting materials, reaction temperature, and type of vessel used for each attempt. The kaolin – Fisher Scientific Lot# 016102, which was used as a starting material in three high-temperature hydrothermal attempts, was sintered at 1400°C (attempt 1), sintered at 600°C (attempt 2), and used as-received (attempt 3). The XRD analysis on all attempts showed vishnevite, $Na_8Al_6Si_6O_{24}(SO_4)\cdot 2H_2O$ and not the desired mineral nosean. Vishnevite is a mineral in the cancrinite group and is a sulfate analogue of cancrinite and hydroxycancrinite.

Table 2-2. Initial Hydrothermal Attempts to Synthesize Nosean

Low Temperature Hydrothermal Method									
Bottle 1				Bottle 2			Reaction Temp (°C)	Vessel	Reaction Time Days
Na_2SO_4 Moles	NaOH Moles	H_2O Moles	Ludox Moles	NaOH Moles	$Al(OH)_3$ Moles	H_2O Moles			
1.00	1.50	33.33	0.20	1.00	0.20	11.11	95	Teflon	7
2.03	1.20	16.67	0.67	0.80	0.33	11.11	95	Teflon	7
1.02	1.20	16.67	0.67	0.80	0.33	11.11	95	Teflon	7
1.00	1.50	16.67	0.20	1.00	0.20	11.11	95	Teflon	7
0.36	1.20	16.67	0.67	0.80	0.33	11.11	95	Teflon	7
0.37	1.50	16.67	0.20	1.00	0.20	11.11	95	Teflon	7
0.28	1.22	16.67	0.67	0.80	0.33	11.11	95	Teflon	7
0.28	1.50	16.67	0.20	1.00	0.20	11.11	95	Teflon	7

Intermediate Temperature Hydrothermal Method									
Bottle 1			Bottle 2		Bottle 3		Reaction Temp (°C)	Vessel	Reaction Time Days
Na_2SO_4 Moles	NaOH Moles	H_2O Moles	H_2O Moles	$NaAlO_2$ Moles	H_2O Moles	$Na_2SiO_2(H2O)_9$ Moles			
0.36	1.50	1.00	0.56	0.020	1.67	0.020	175	Auto-clave	7

High Temperature Hydrothermal Method							
Na_2SO_4 Moles	Kaolin Moles	Molecular Sieve 4A Moles	Molecular Sieve 13X Moles	NaOH	Reaction Temp (°C)	Vessel	Reaction Time Days
0.14	0.04			110 mL 8M	225	Auto-clave	7
0.14	0.04			110 mL 8M	225	Auto-clave	7
0.50	0.05			125 mL 8M	225	Auto-clave	7
0.50		0.06		125 mL 8M	225	Auto-clave	7
0.14			0.0005	110 mL 8M	225	Auto-clave	7

Other attempts at synthesizing nosean were conducted using solid-state reaction as outlined in Table 2-3. Table 2-3 shows the different starting compounds, reaction temperature, and reaction times for all the solid-state reactions. All of the solid-state reactions ended with extra peaks in the XRD analysis. Phase-pure nosean was not fabricated until the starting compounds were first dissolved, dried, and heated.

Table 2-3. Initial Solid-State Reaction Attempts to Synthesize Nosean

Attempt	Na_2SO_4 Moles	Kaolin Moles	$NaHCO_3$ Moles	Ludox Moles	Molecular Sieve 4A Moles	$Al(OH)_3$ Moles	Reaction Time and Temperature
1	0.009	0.027	0.054				82 hrs @725°C, 36 hrs @800°C, 84 hrs @825°C, 56 hrs @900°C
2	0.027	0.027	0.054				490 hrs @800°C
3	0.090	0.027	0.054				490 hrs @800°C
4	0.027		0.054		0.003		358 hrs @800°C
5	0.090		0.054		0.003		348 hrs @800°C
6	0.090	0.027					327 hrs @800°C
7	0.027	0.027	0.054				82 hrs @725°C, 36 hrs @800°C, 84 hrs @825°C, 56 hrs @900°C
8	0.018	0.027	0.054				82 hrs @725°C, 36 hrs @800°C, 84 hrs @825°C, 56 hrs @900°C
9	0.027	0.027	0.040				82 hrs @725°C, 36 hrs @800°C, 84 hrs @825°C, 56 hrs @900°C
10	0.030		0.0298	0.0303		0.0301	82 hrs @725°C, 36 hrs @800°C, 84 hrs @825°C, 56 hrs @900°C
11	0.010		0.0298	0.0303		0.0301	82 hrs @725°C, 36 hrs @800°C, 84 hrs @825°C, 56 hrs @900°C

The initial synthesis of Cl-sodalite was started with the same process as the nosean fabrication: a low- and a high-temperature hydrothermal method. Both recipes were adjusted several times and each used an excess amount of sodium chloride and sodium hydroxide, which was washed out. Table 2-4 outlines the different starting materials, reaction temperature, and type of vessel used for each attempt. The kaolin, which is the same kaolin used for the nosean synthesis, was used as a starting material in three high-temperature hydrothermal attempts. It was sintered at 1400°C (attempt 1), sintered at 600°C (attempt 2), and used as-received (attempt 3). Cl-sodalite was made using both techniques, but extra peaks were observed and there were crystallite size differences. The low-temperature hydrothermal method had broad peaks indicating small crystallite size while the high-temperature hydrothermal method showed narrow sharp peaks indicating large crystallite size. Once a recipe for the Cl-sodalite was developed that was phase-pure and had large crystallite size, it was adopted for all the other sodalites.

Table 2-4. Initial Hydrothermal Attempts to Synthesize Cl-Sodalite.

Low Temperature Hydrothermal Method									
NaCl Moles	NaOH Moles	H_2O Moles	Ludox Moles	NaOH Moles	$Al(OH)_3$ Moles	H_2O Moles	Reaction Temp. °C	Vessel	Reaction Time Days
1.50	1.50	25.00	0.20	1.00	0.30	11.11	95	Teflon	7
1.00	1.46	18.33	0.40	0.70	0.30	6.39	95	Teflon	7
1.67	1.20	16.67	0.67	0.80	0.33	11.11	95	Teflon	7

High Temperature Hydrothermal Method						
NaCl Moles	Kaolin Moles	Molecular Sieve 4A Moles	NaOH	Reaction Temp. °C	Vessel	Reaction Time Days
0.29	0.04		110mL 8M	225	autoclave	7
0.29	0.04		110mL 8M	225	autoclave	7
0.51	0.05		125mL 8M	225	autoclave	7
0.51		0.006	125mL 8M	225	autoclave	7

All the starting materials for the various phase-pure standards are listed in Table 2-5 below.

Table 2-5. Starting Materials

Compound	Formula	Manufacturer	Part #	Lot #
Aluminum Hydroxide	AlH_3O_3	Sigma Aldrich	239186-500G	11515KA
Ludox®HS-400 colloidal silica, 40wt% suspenison in water	SiO_2	Sigma Aldrich	420816-4L	06914BH
Molecular Sieve 4A Powder <5micron activated	$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot XH_2O$	Aldrich	233668-500G	07328DB
Sodium Aluminum Oxide	$NaAlO_2$	Alfa Aesar	C17N38	35453
Sodium Chloride	NaCl	Fisher Scientific	S271-500	991967
Sodium Iodide	NaI	Fisher Scientific	21738-2.5Kg	MKAA0911
Sodium Perrhenate	NaReO4	Alfa Aesar	11412	B08L39
Sodium Sulfate Decahydrate	$Na_2SO_4 \cdot 10H_2O$	Fisher Scientific	S419-500	75817

2.2 Successful Nepheline Synthesis

Nepheline was synthesized by a solid-state reaction using the Molecular Sieve 4A powder, Zeolite A. Several 95%Pt – 5%Au crucibles containing the molecular sieve 4A powder were placed inside of the CM Inc. high temperature furnace. Table 2-6 outlines how the furnace was programmed for each heating cycle. After each heating cycle, the material was removed from the 95%Pt – 5%Au crucibles, and ground using a well-cleaned agate mortar and pestle to prevent contamination from occurring.

Table 2-6. Furnace Conditions for Nepheline Synthesis

	Ramp Rate °C/min	Temperature °C	Dwell Time hrs
Heating Cycle 1	5	1000	6
Heating Cycle 2	5	1050	4
Heating Cycle 3	5	1100	4

2.3 Successful Nosean Synthesis

Nosean was prepared using components outlined in Table 2-7 using a modified solid-state reaction where the starting materials were dissolved in deionized water and dried before heating. Sixty small batches were prepared to produce the 200 grams needed. The recipe in Table 2-7 by design had an excess amount of sodium sulfate which was washed out in the final step of the synthesis.

Table 2-7. Nosean Recipe

Na_2SO_4 Moles	Ludox Moles	$NaAlO_2$ Moles
0.0303	0.0303	0.0303

The following is the step-by-step process to synthesize nosean:

- Dry the sodium sulfate decahydrate (see Table 2-5) at 105°C over night in a Blue M Lindberg drying oven to remove the waters of hydration. (The sodium aluminum oxide in Table 2-5was also dried for several hours at 105°C)
- Grind the dried sodium sulfate using an agate mortar and pestle to the consistence of flour (Place the ground sodium sulfate into a desiccator to prevent the re-adsorption of water.)
- Weigh out the dried sodium sulfate and the sodium aluminum oxide according to Table 2-7, and pour the material into a Teflon™ beaker.
- Add approximately 150-mL of deionized water to the Teflon™ beaker to dissolve the sodium sulfate and sodium aluminum oxide, and mix for 10 minutes.
- Weigh out the Ludox®, and pour it into the Teflon™ beaker.
- Place the Teflon™ beaker into a Blue M Lindberg drying oven at 105°C overnight.
- Remove the dried material from the Teflon™ beaker, and grind it in an agate mortar and pestle.
- Place the ground material into 95%Pt – 5%Au crucibles.

Twenty 95%Pt – 5%Au crucibles were placed inside a Thermolyne 46100 high-temperature furnace at a time. Table 2-8 outlines how the furnace was programmed for each heating cycle. After each heating cycle, the material was removed from the 95%Pt – 5%Au crucibles, and ground using an agate mortar and pestle to prevent contamination from occurring.

Table 2-8. Furnace Conditions for Nosean Synthesis

	Ramp Rate °C/min	Temperature °C	Dwell Time hrs
Heating Cycle 1	5	900	90
Heating Cycle 2	5	900	56

After the second heating cycle, the material was ground into a fine powder, and poured into a 250-mL Nalgene bottle with 100 mL of deionized-water. The mixture was shaken vigorously and poured into a Fisher Scientific glass microanalysis vacuum filter assembly with a 0.46 μm Millipore filter. The material was washed with copious amounts of deionized water to remove the excess sodium sulfate from the nosean, and dried in a Blue M Lindberg drying oven set at 105°C overnight. XRD analysis was conducted on the solids to verify that the washing process removed all of the sodium sulfate.

2.4 Successful Sodalite Synthesis (Re, I, Cl, Tc-Re)

The mineral sodalite consists of a framework of alternating SiO_4 and AlO_4 tetrahedra that form an aluminosilicate cage having "window pane" openings of 2.6Å. This cage opening in the sodalite structure is where the anions such as Cl^-, I^-, ReO_4^-, and TcO_4^- will be atomically bonded to the Al, Si, and Na. A hydrothermal technique was used to synthesize the four sodalites. Six Paar Instruments Inc. #452 HC 316 stainless steel pressure vessels (Figure 2-1) with Teflon™ liners were charged according to Table 2-9. These vessels manufactured in 1986 were stamped with a maximum operating pressure of 3,000-psig @ 350°C. The six vessels were placed in a Blue M Lindberg drying oven at 225°C for 7 days. The six pressure vessels were charged three times each for each of the rhenium, iodide, and chloride sodalite standard fabrications.

Table 2-9. Re, I, and Cl Sodalite Recipe

$NaReO_4$/NaI/NaCl Moles	Molecular Sieve 4A Moles	NaOH
0.29	0.004	110 mL of 8M

The Teflon™ liners were removed from the cooled pressure vessels, and the hydroxide solution was slurried off. The solids were rinsed into six 250-mL Nalgene bottles with deionized water. As the initial step to drop the pH of the solids to between 7 to 8, the Nalgene bottles were placed inside of a Fisher Scientific Marathon 22K centrifuge. The solids were spun down at 4500 rpm for 15 minutes. The liquid was slurried off and more deionized water was added. The process of rinsing the solids was repeated several times. The pH-adjusted solids were poured into several evaporating dishes, and dried overnight at 105°C. XRD analysis was conducted on each batch to confirm that the particular pure-phase sodalite was fabricated before combining all the batches together.

Figure 2-1. Parr Pressure Vessel

To determine if a technetium sodalite could be fabricated, several initial tests were performed. These tests included the following:

- converting ammonium perrhenate to sodium perrhenate to Re-sodalite
- reducing the amount of sodium perrhenate to fabricate Re-sodalite
- using sodium permanganate as a surrogate for technetium to fabricate a Mn-Re sodalite.

The method to convert ammonium perrhenate to sodium perrhenate consisted of adding 49.6mL of 0.9M NaOH and 150mL of DI-water to 12g of ammonium perrhenate. This mixture was added to a Teflon™ liner. The Teflon™ liner was placed inside of a drying oven which was set at 105°C for 24 hours. The Teflon™ liner was removed from the drying oven and set aside to cool down to room temperature. Next, the Teflon™ liner was charged according to Table 2-10 to synthesize Re-sodalite, and placed inside the Parr pressure vessel.

Table 2-10. Re-Sodalite Recipe

$NaReO_4$ Moles/Grams	Molecular Sieve 4A Moles/Grams	NaOH
0.0439/12.0000	0.0006/1.3274	16.66 mL of 8M

The pressure vessel was placed in a Blue M Lindberg drying oven at 225°C for 7 days. After the seven days, the solids were removed from the Teflon™ liner, and washed as described above to drop the pH. The amount of remaining solids from the synthesis was approximately 1.5g. Figure 2-2 shows the XRD analysis of a subsample from the 1.5g of washed solids.

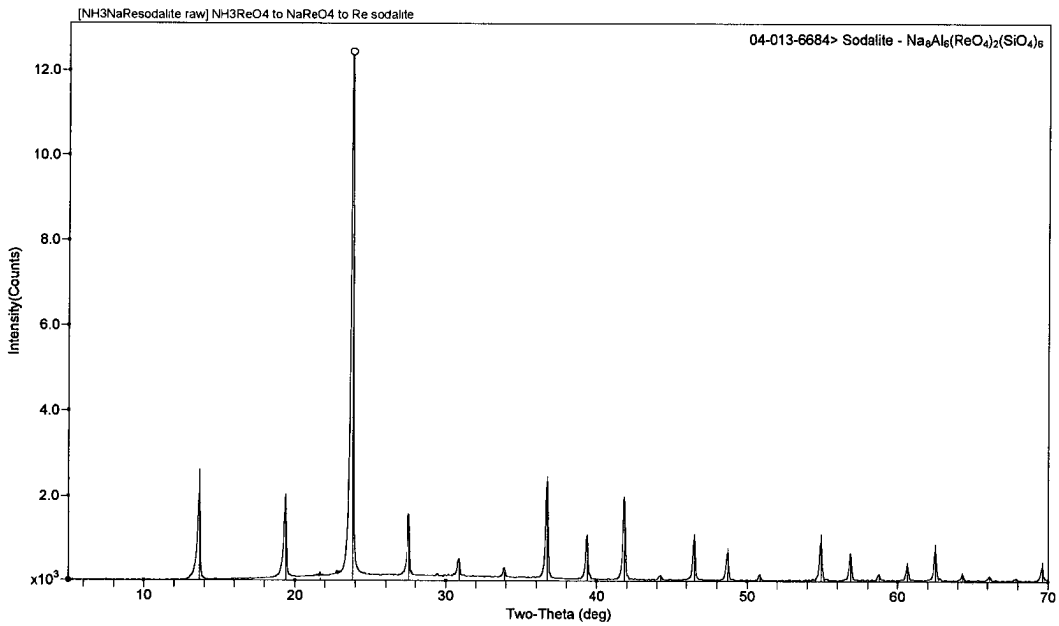

Figure 2-2. XRD analysis of Re-Sodalite starting with 12-g of ammonium perrhenate

The second test to reduce the amount of sodium perrhenate starting material was two-fold. On one hand, the least amount of the sodium perrhenate needed to produce Re-sodalite was determined. On the other hand, by reducing the starting sodium perrhenate, the small amount of the technetium that was on-hand was concentrated into a mixed Re/Tc-sodalite structure. Two Paar pressure vessels with Teflon™ liners were charged according to Table 2-11. The two vessels were placed in a Blue M Lindberg drying oven at 225°C for 7 days.

Table 2-11. Re-Sodalite Recipe

$NaReO_4$ Moles/Grams	Molecular Sieve 4A Moles/Grams	NaOH
0.0110/3.0000	0.00015/0.3319	4.17 mL of 8M
0.0220/6.0000	0.00030/0.6637	8.33 mL of 8M

The solids from both attempts were washed according to the above directions. The first attempt, which had 3.0g of sodium perrhenate starting material, did not produce solids. The second attempt however did. The amount of solids that was recovered from the washings was 0.75g. An XRD analysis was conducted to ensure Re-sodalite was synthesized. Figure 2-3 shows the XRD analysis.

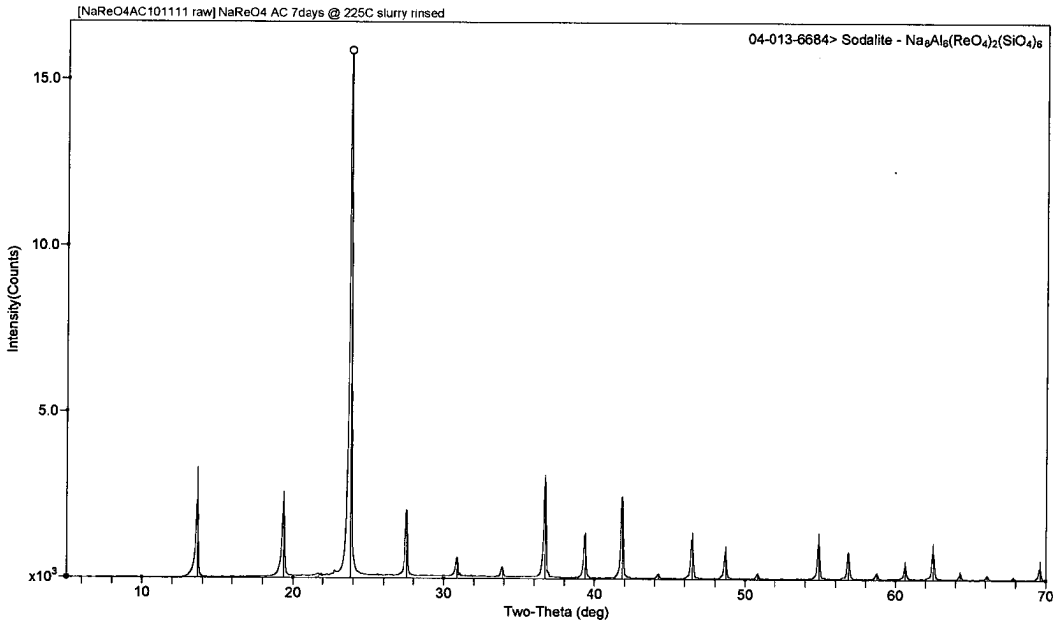

Figure 2-3. XRD analysis of Re-Sodalite starting with 6-g of sodium perrhenate

The final test was to use sodium permanganate as a surrogate for the ammonium pertechnetate in the fabrication of a mixed Mn-Re sodalite. One of the pressure vessels with a Teflon™ liner was charged according to Table 2-12.

Table 2-12. Re-Mn Sodalite Recipe

$NaReO_4$ Moles/Grams	$NaMnO_4$ Moles/Grams	Molecular Sieve 4A Moles/Grams	NaOH
0.02/5.60	0.0028/0.40	0.00032/0.7047	8.85 mL of 8M

The pressure vessel was placed in a Blue M Lindberg drying oven at 170°C for 16 days. (An attempt was made to synthesize the Mn-Re sodalite at 225°C, but at elevated temperatures the manganese changes oxidation states.) The solids were washed in the same fashion as the Cl, I, and Re sodalites. A subsample was taken from the washed solids to perform XRD and SEM analysis. The XRD spectrum is shown in Figure 2-4 and contains a sodalite phase plus a sodium manganese oxide hydrate phase. The SEM-EDS analysis confirms that the sodalite synthesized does contain Mn and Re. The results of the SEM analysis are shown in Figure 2-5 and Figure 2-6.

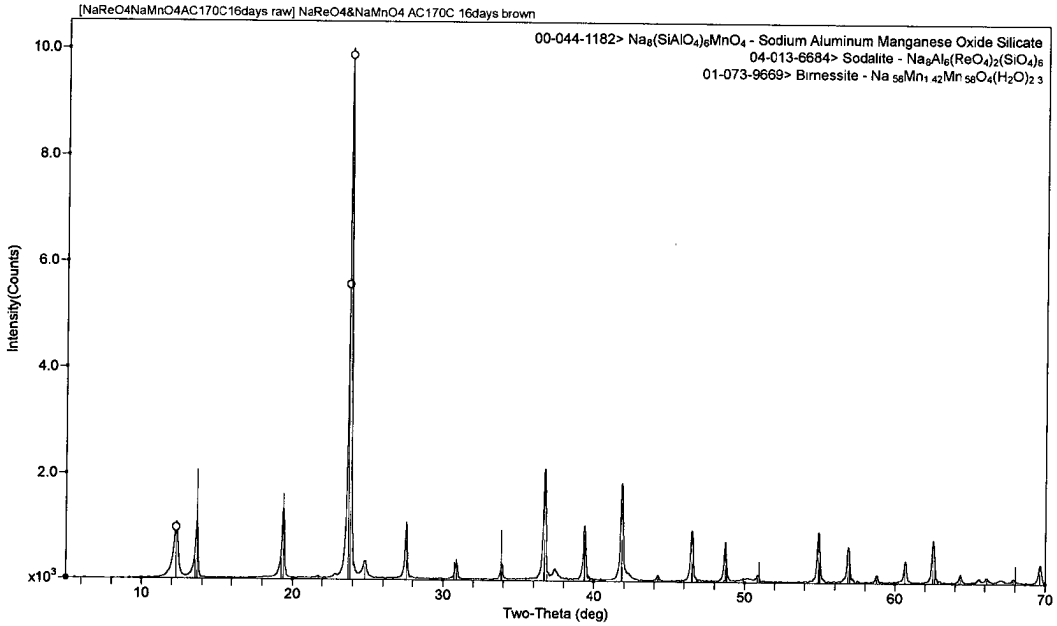

Figure 2-4. XRD analysis of Mn-Re Sodalite

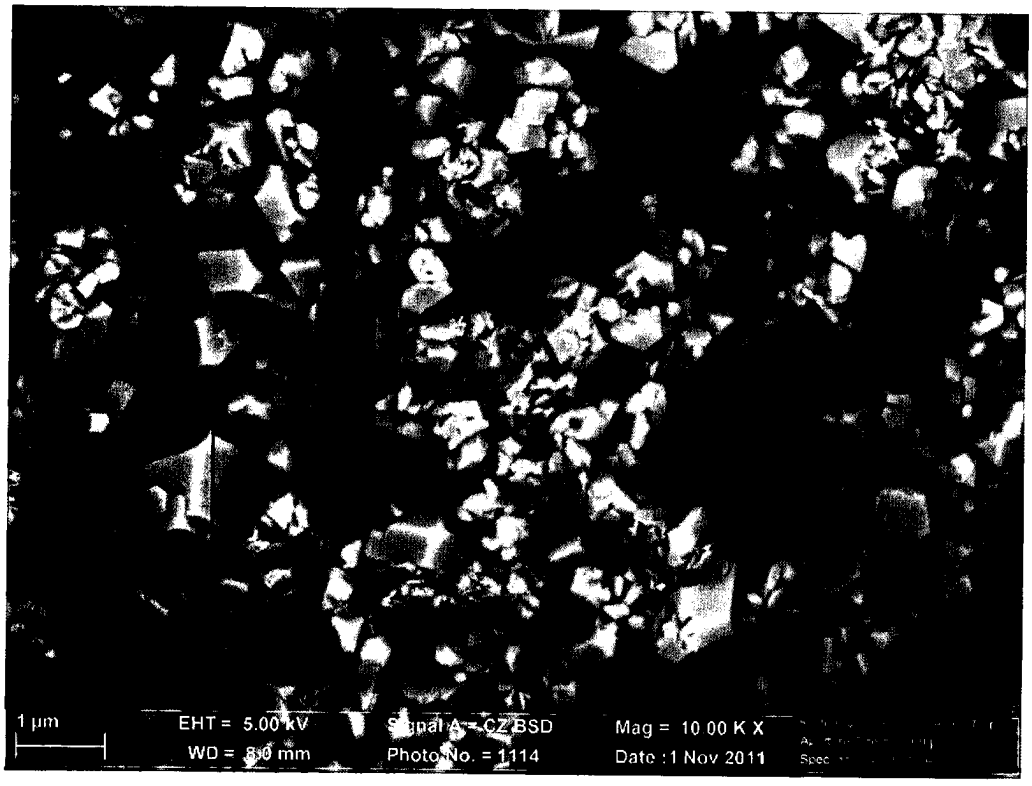

Figure 2-5. SEM photograph showing the Mn-Re sodalite crystals.

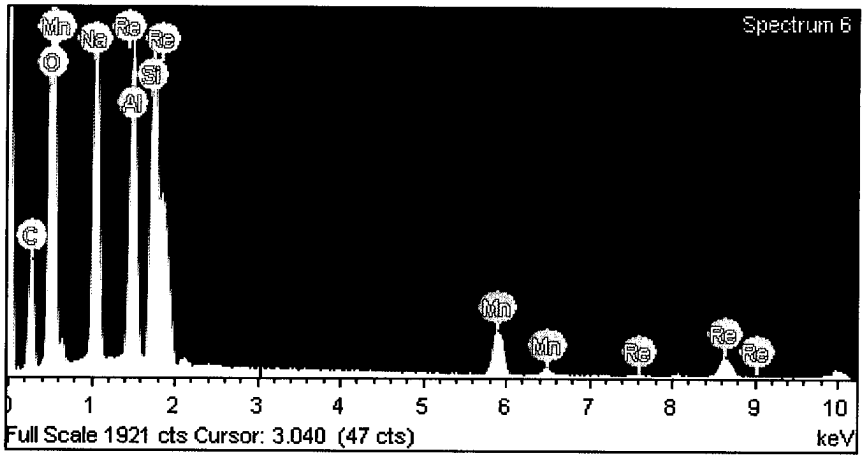

Figure 2-6 . SEM-EDS analysis of the Mn-Re sodalite.

The Tc-Re sodalite was synthesized using a two-step process. The first step was to convert the ammonium pertechnetate to sodium pertechnetate. This was accomplished by adding 1.41 mL of 0.9M NaOH and 4.26 mL of DI-water to 0.34 g of ammonium pertechnetate to one of the Teflon™ liners. The Teflon™ liner was placed inside of a drying oven, which was set at 105°C, for 24 hours. This work was conducted in a radiological hood. The Teflon™ liner was removed from the drying oven and set aside to cool down to room temperature. Next, the Teflon™ liner was charged according to Table 2-13 to synthesize Tc-Re sodalite, and placed inside the Parr pressure vessel.

Table 2-13. Tc-Re Sodalite Recipe

$NaReO_4$ Moles/Grams	NaTcO4 Moles/Grams	Molecular Sieve 4A Moles/Grams	NaOH
0.021/5.6600	0.0019/0.34	0.00032/0.6829	8.57 mL of 8M

The pressure vessel was placed in a Blue M Lindberg drying oven at 225°C for 8 days. After the eight days, the solids were removed from the Teflon™ liner, and washed using a Fisher Scientific glass microanalysis vacuum filter assembly with a 0.5 μm Millipore Teflon™ filter. The solids were washed with DI water until the pH of the solution dropped between 7 to 8. The washed solids were place inside of a drying oven at 105°C overnight. The amount of solids obtained from the synthesis was 0.68 g. XRD and SEM analysis were conducted on the dried solids to confirm that a mixed Tc-Re sodalite was synthesized.

2.5 X-ray Diffraction Analysis

The samples were ground for 5 minutes in an agate mortar and pestle using ethanol as a lubricant to facilitate grinding. Ground powder was smeared and fixed to a square glass slide using a 1:10 collodion/amyl acetate mixture. X-ray diffraction data were collected on a Bruker theta-2theta D8 Advance X-ray Diffractometer. The instrument was step scanned over a 5-70° 2Θ range with

a 0.02° step size and a dwell time of 1s for a total measurement time of ~60 min. A detailed compilation of all the instrument parameters is included in Table 2-14. Compound search-match identification was performed with Jade™ software (Version 9.1) from Materials Data Inc. using the inorganic powder diffraction file PDF4™ powder diffraction database from the International Centre for Diffraction Data (ICDD). A typical layout for the x-ray diffractometer is shown in Figure 2-7, where DS is the divergence slit, AS is an antiscatter slit (either diffracted side or detector antiscatter), SS is a soller slit (either divergence [primary] and/or diffracted [secondary] sides), and RS is the receiving slit.

Table 2-14. Instrument Parameters

Radiation Source	CuKα
X-ray Source Power	45kV,40mA
Wavelength	1.5405982 Å
Goniometer	Bruker D8
Divergence Soller Slit	None
Divergence Slit	1°
Divergence Antiscatter	1°
Specimen Rotation	No
Diffracted Beam Antiscatter	1°
Diffracted Beam Soller	1°
Secondary Monochromator	Curved pyrolytic graphite
Receiving Slit	0.15°
Detector	NaI Scintillation
2θ Range	5° - 70°
Step Size	0.02° (2θ)
Time per Step	1 s

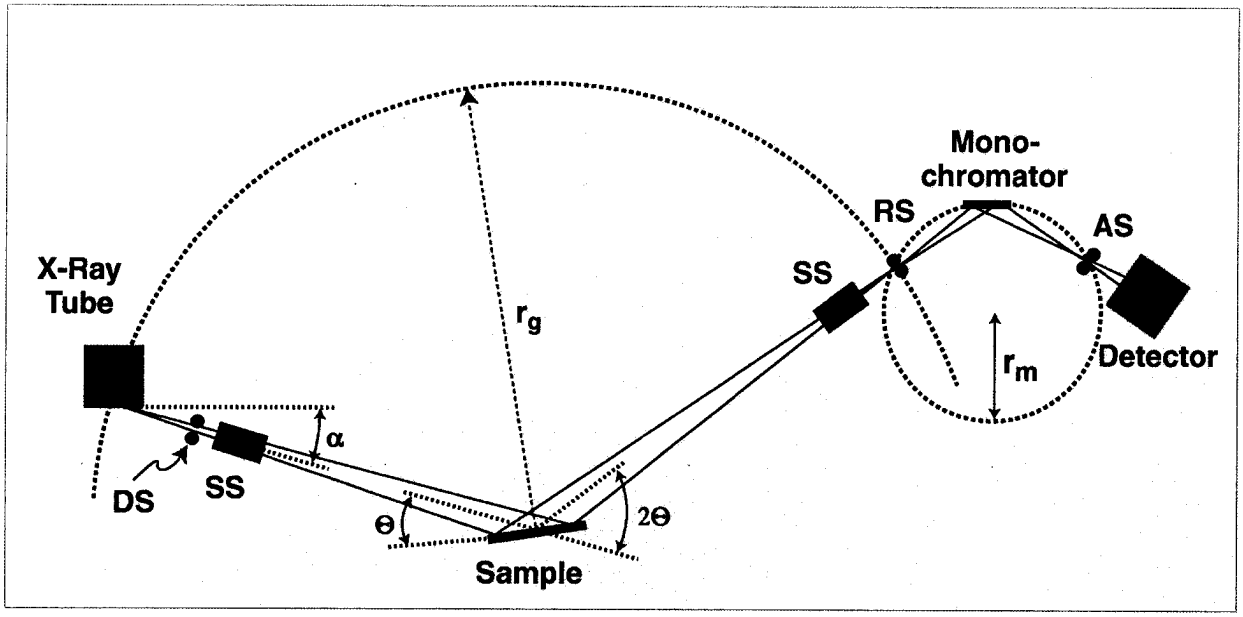

Figure 2-7. Typical X-ray Diffractometer Configurations

2.6 Particle Size Analysis

The Microtrac S3500 particle size analyzer uses a wet sample delivery controller (recirculator) to disperse the sample uniformly in a fluid and deliver the sample to the analyzer. This wet sample delivery controller in its basic form consists of a reservoir where the sample is introduced, a fluid pump, a valve to the drain system, and the necessary tubing connections to the analyzer. The flow through the analyzer sample cell is always from the bottom to the top. The analyzer consists of the sample cell and three lasers (improves resolution) and two silicon photodiode array detectors. Figure 2-8 depicts the top-down view showing the positions of the lasers and detectors.

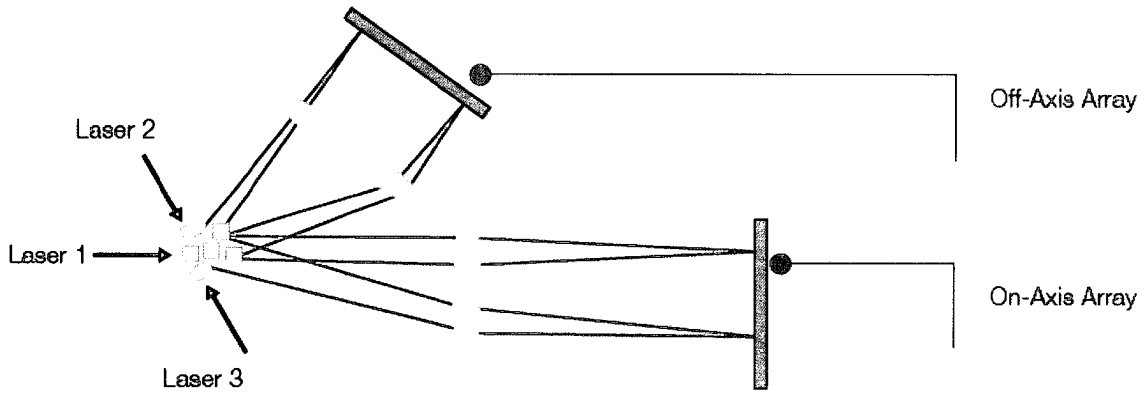

Figure 2-8. Top-down view showing the optical configuration of the Microtrac S3500

A laser beam is projected through the sample cell that contains a stream of moving particles suspended in a liquid. Light rays that strike a particle are scattered (Mie scattering, where the particle radius ≈ laser wavelength.). The scattered light forms an angular pattern which is measured by the two photodiode arrays. Electrical signals proportional to the measured light intensities are then processed by the computer using modified Mie calculations for non-spherical particles to form a multichannel histogram of the particle size distribution.

The required mass to obtain an average sample loading index on the Microtrac S3500 varies with particle size, i.e., the finer the particles size distribution, the smaller the mass needed. Approximately, 0.5 g of each pure-phase standard was pulled in duplicate and was placed into labeled 4-dram vials. Deionized water was added to each of the 4-dram vials along with 1 mL of 4% sodium hexametaphosphate. Sodium hexametaphosphate is used as a dispersing agent. Each 4-dram bottle was rotated in a figure-eight pattern to ensure complete dispersion of the particles before a slurry was pulled to be analyzed. A complete list of all the instrument operating parameters can be found in Table 2-15.

Table 2-15. S3500 Instrument Parameters for Particle Size Measurements

Transparency	Absorbing
Particle Shape	Irregular
Particle Refractive Index	NA
Number of Channels	103
Progression	Geom 8 Root
Residuals	Disabled
Filter	Enabled
Fluid	Water

2.7 Surface Area Analysis

The Micromeritics ASAP 2020 is an automated apparatus for measuring adsorption isotherms and calculating surface area and total pore volume. Although the ASAP 2020 is capable of measuring the total pore volume in a sample, the primary function of the ASAP 2020 is to determine the surface area of solid materials using either the single- or multiple-point methods. The instrument is configured to measure adsorption and desorption isotherms with nitrogen (total sample surface area >10 m^2), argon (total sample surface area >5 but <10 m^2), or krypton (total sample surface area < 5 m^2) at liquid nitrogen temperature.

The instrument uses a flowing-gas technique in which the analysis gas (nitrogen/argon/krypton) flows into a tube containing the sample and into a balance tube at the same time (Figure 2-9). The internal volume and the temperature surrounding both tubes are identical. The only difference is the presence of the sample in the sample tube.

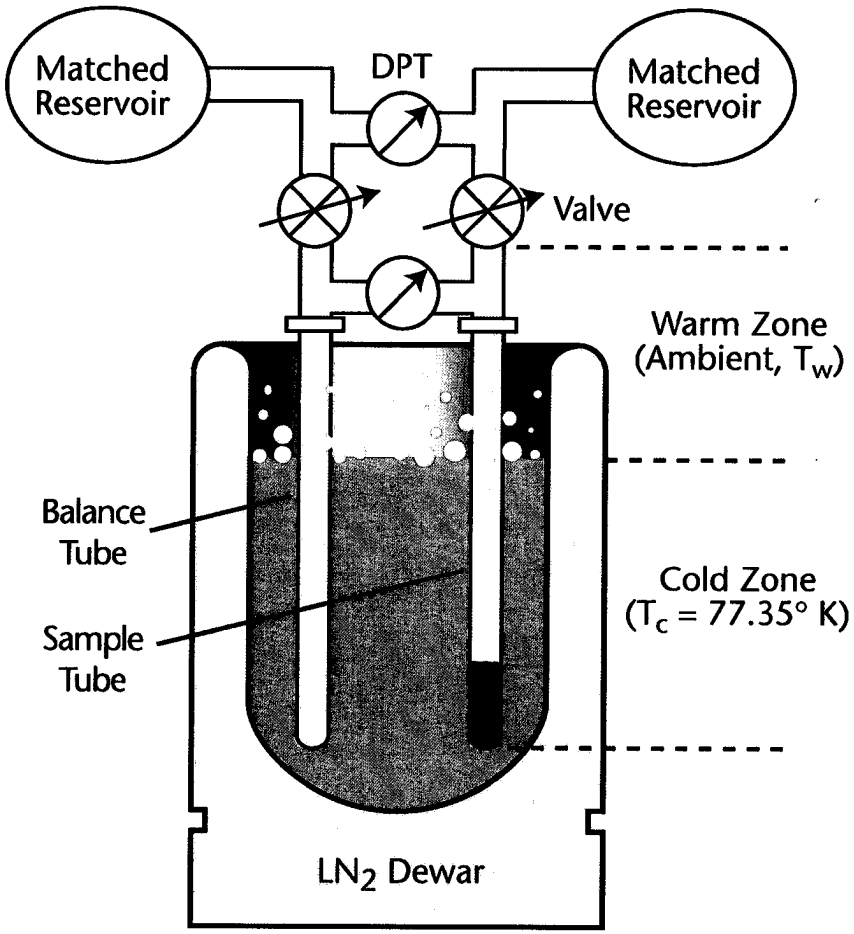

Figure 2-9. Schematic representation of the ASAP 2020 system

The sample and balance tubes are immersed in a single liquid nitrogen bath, which maintains isothermal conditions for both tubes. By using this configuration, the liquid nitrogen level in the Dewar does not need to be kept constant. Any change in the location of the warm and cold zones on the balance and sample tubes is exactly the same. Nitrogen gas is delivered to the sample tube by a servo valve mechanism. The delivery rate of nitrogen gas flow into the balance tube is controlled by another servo valve connected to a differential pressure transducer (DPT). This differential pressure transducer measures the pressure imbalance between the sample and balance tubes, which is caused by the adsorption of the nitrogen onto the sample. As the sample adsorbs nitrogen, the pressure drops in the sample tube. The servo valve continuously restores the pressure balance between two tubes by admitting more gas into the sample tube. The ASAP 2020 maintains a constant pressure of nitrogen over the sample while varying the rate of analysis gas delivery to exactly match the rate at which the sample can adsorb the gas. Helium is used for free-space (headspace or dead-space) measurement to determine any slight difference in volume between the balance tube and the sample tube because of sample displacement[10]. Filler rods are routinely inserted into the two tubes to reduce the free space, which results in better precision and more accurate surface areas.

Prior to adsorption isotherm measurement, physiosorbed contaminants (moisture, oxygen, carbon dioxide, and various organic molecules) are removed from the sample surface by degassing at an elevated temperature under vacuum on the degas side of the ASAP 2020. The degas temperature

selected must be a compromise - high enough to provide sufficient energy to the molecules to overcome the attractive forces to the adsorbent and to minimize out-gassing time, yet not change its surface area or porosity.

The amount of material used for the surface area measurement varied between 2.5 to 3.2g for nosean and the sodalite standards to 1 to 2g for the nepheline standard. The weighed out material for each standard was added to sample tubes and degassed using the parameters listed in Table 2-16. After the surface contaminants were removed, the glass tube and sample were weighed and a filler rod was added to each glass sample tube except the tube containing the nepheline standard. The nepheline standard was run using krypton gas and a filler rod was not required. The glass sample tubes were placed on the analysis port of the ASAP 2020. Nineteen adsorption points using nitrogen as the absorbate and nine adsorption points using krypton as the absorbate were measured to cover the entire BET range. For the nosean and sodalites, 14 - 15 of these 19 adsorption points were used to generate a linear BET plot with a correlation coefficient > 0.9999 whereas 8 of the 9 absorption points were used for the nepheline.

Table 2-16. Instrument Parameters for Surface Area Measurements

Degassing	
Sample Weight	~1.4-g Nepheline 2.5- 3.0-g Nosean 2.5 -3.2-g Sodalite
Gas	N_2 (99.995%)
Gas Pressure	17- psi
Time and Temperature	Nepheline: 6 to 17-hr @ 440 °C Nosean: 4-hr @ 150 °C Sodalite: 4-hr @ 200 °C
Surface Area Measurement	
Model	Micromeritics ASAP 2020
Adsorption Gas	Kr (99.995%), N_2 (99.995%)
Gas Pressure	17-psi
Evacuation time	1-hr for Krypton, 10-min for Nitrogen
1st Relative Pressure	0.05 P/P_0 for Krypton, 0.01 P/P_0 for Nitrogen
Last Relative Pressure	0.3 P/P_0 for both gases
Adsorption Points	9 for Krypton, 19 for Nitrogen
Equilibration time	Nepheline: 10-s Nosean and Sodalites: 15-s

3.0 Results and Discussion

All the pure-phase standards with the exception of nepheline were fabricated in small batches. These small batches ranged in size between 4 and 5 g for nosean and between 7 and 12 g for the sodalites. As discussed earlier, the batches were hand ground in an agate mortar and pestle to prevent any contamination from any mechanical grinding machine. The small batches were combined into a 1-L Nalgene polyethylene bottle, and mixed for 10 to 15 minutes using a figure-eight motion. Each standard was split (160 g/40 g) with 160 g being sent to ORNL for the single-pass flow-through testing and thermodynamic data development. XRD, particle size, and surface area measurements were conducted on the other 40 g. The XRD analysis of each standard is shown in Figure 3-1 through Figure 3-5. The particle size and surface area measurements were done in duplicate, and the results are shown in Table 3-1 and Table 3-2. The particle size measurements are an average of three 30-second runs (See Appendix for the particle size plots)

The Tc-Re sodalite was fabricated based on concentrating the amount of technetium that would go into a sodalite structure with the least amount of starting material that would produce a sodalite mineral. The total amount of Tc-Re sodalite produced was 0.68 g. The XRD analysis of this mixed sodalite standard is shown in Figure 3-6. Since no PDF card exists for the Tc-sodalite, the spectrum was labeled with the PDF card for Re-sodalite. The XRD analysis was not able to show that the technetium went into the sodalite structure, but was able to show that the solids were a single phase. The SEM-EDS analysis shown in Figure 3-7 and Figure 3-8 confirms that some of the technetium was incorporated into the sodalite structure. This material will be packaged and shipped to ORNL for more analyses.

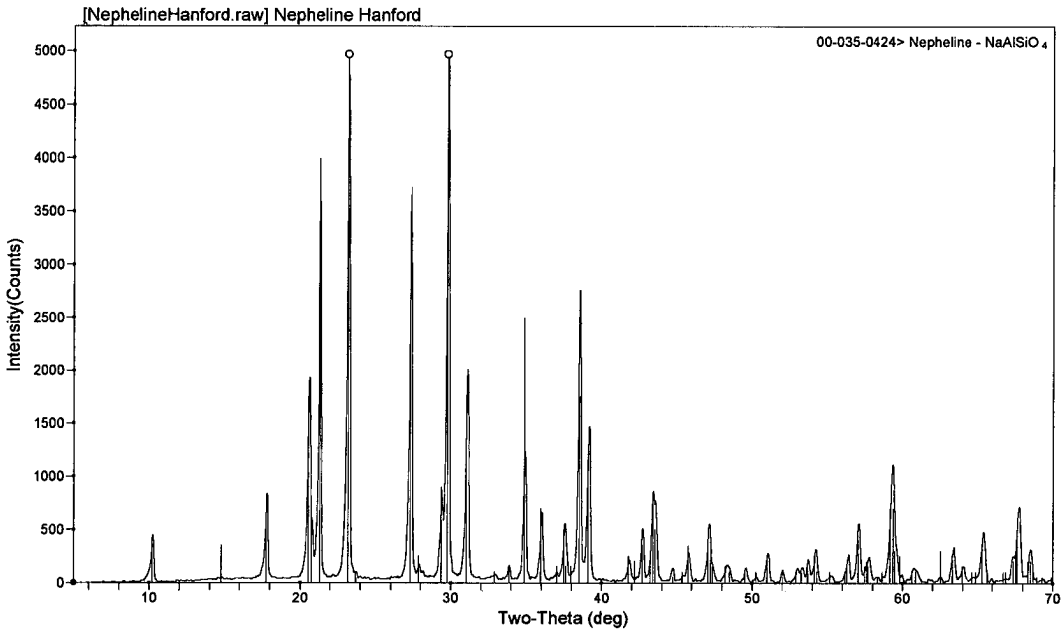

Figure 3-1. XRD analysis of Nepheline

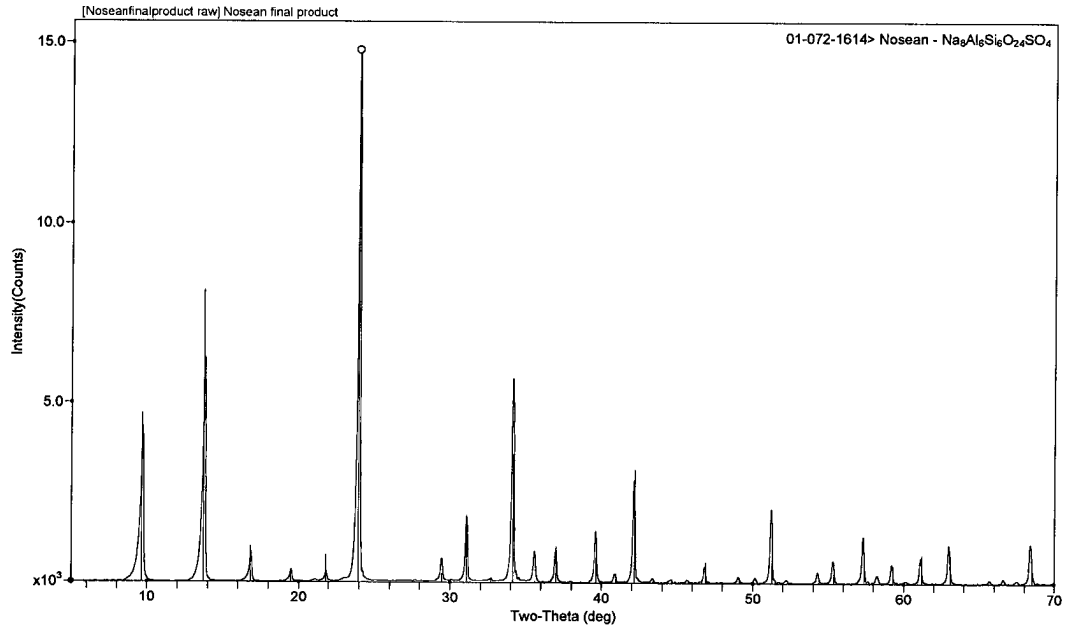

Figure 3-2. XRD analysis of Nosean

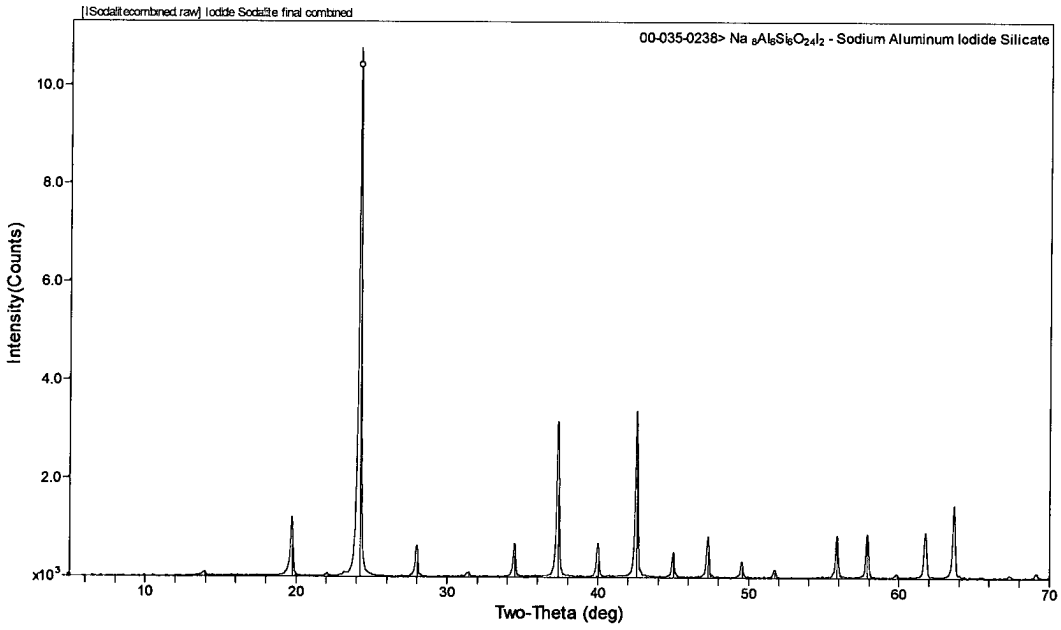

Figure 3-3. XRD analysis of I-Sodalite

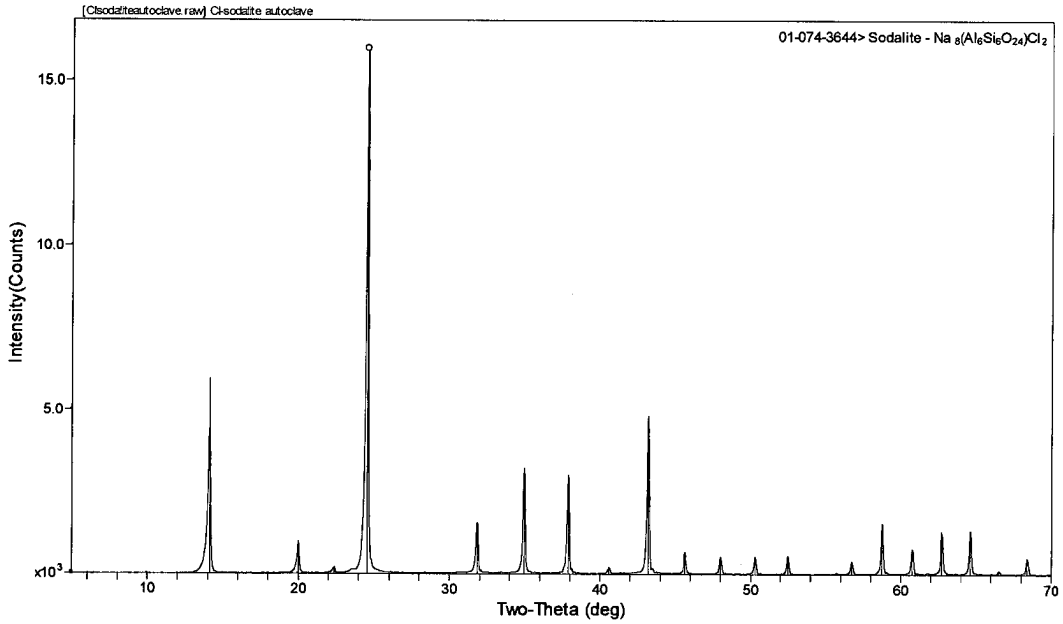

Figure 3-4. XRD analysis of Cl-Sodalite

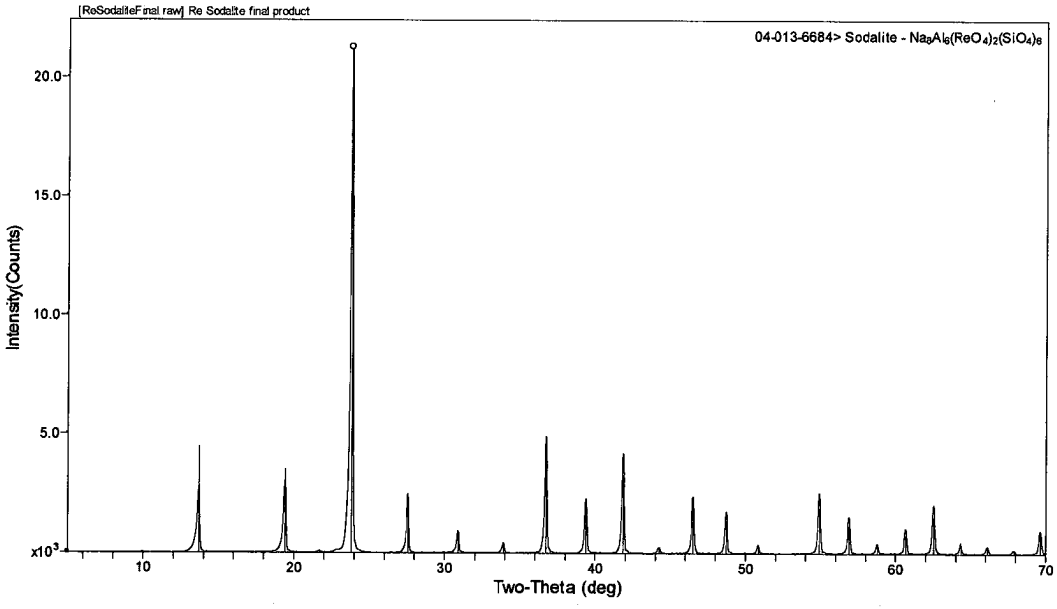

Figure 3-5. XRD analysis of Re-Sodalite

Table 3-1. BET Surface Area Measurements Results

	Sample A m^2/g	Sample B m^2/g
Nepheline	1.01	1.03
Nosean	2.59	2.72
I-Sodalite	7.21	7.22
Cl-Sodalite	7.95	7.95
Re-Sodalite	3.09	3.07

Table 3-2. Particle Size Measurements Results (Mean Volume Distribution)

	Nepheline		Nosean		I-Sodalite	
Percentile	Sample A Size (µm)	Sample B Size (µm)	Sample A Size (µm)	Sample B Size (µm)	Sample A Size (µm)	Sample B Size (µm)
10	5.19	5.03	10.18	11.01	0.685	0.692
16	10.01	9.65	18.07	19.22	0.917	0.943
25	21.73	20.60	32.27	33.95	1.366	1.417
40	51.20	49.33	62.14	64.73	2.029	2.067
50	73.54	71.18	89.49	93.28	2.416	2.445
60	100.9	98.34	126.1	130.4	2.829	2.850
70	134.3	133.0	167.6	170.7	3.33	3.35
75	152.8	152.6	189.1	191.2	3.65	3.68
90	222.5	225.5	268.5	268.4	5.94	6.43
95	264.2	268.1	316.2	315.5	10.82	18.86

	Cl-Sodalite		Re-Sodalite	
Percentile	Sample A Size (µm)	Sample B Size (µm)	Sample A Size (µm)	Sample B Size (µm)
10	0.720	0.732	0.902	0.831
16	0.938	0.977	1.204	1.100
25	1.297	1.375	1.670	1.539
40	1.845	1.960	2.472	2.312
50	2.197	2.334	3.06	2.870
60	2.587	2.763	3.72	3.851
70	3.07	3.33	4.51	4.27
75	3.39	3.71	4.95	4.74
90	5.27	6.74	6.84	7.16
95	7.2	11.15	8.13	9.35

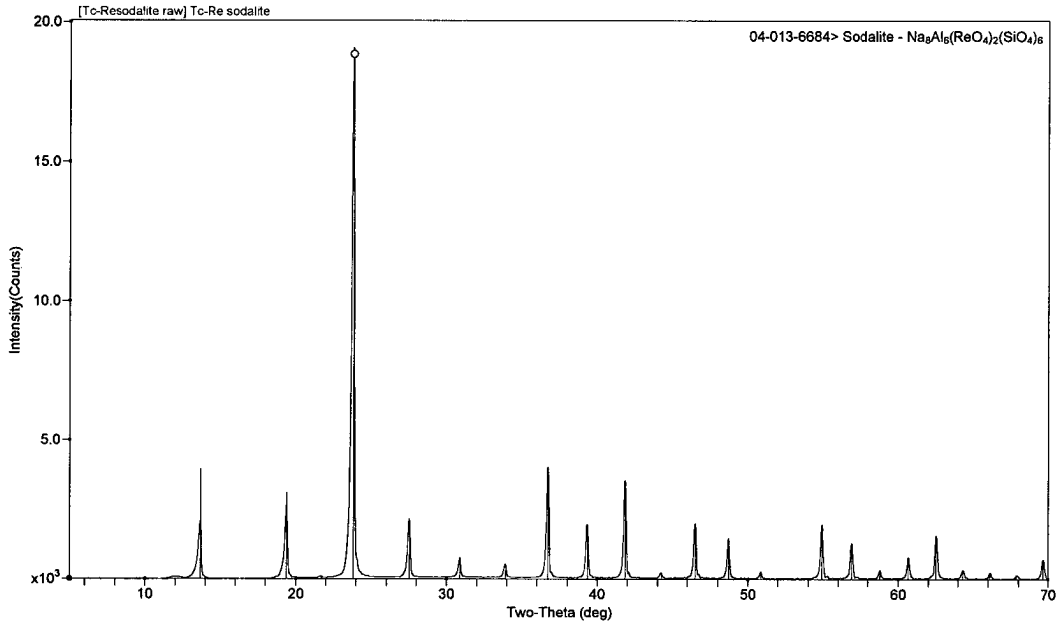

Figure 3-6. XRD analysis of Tc-Re Sodalite

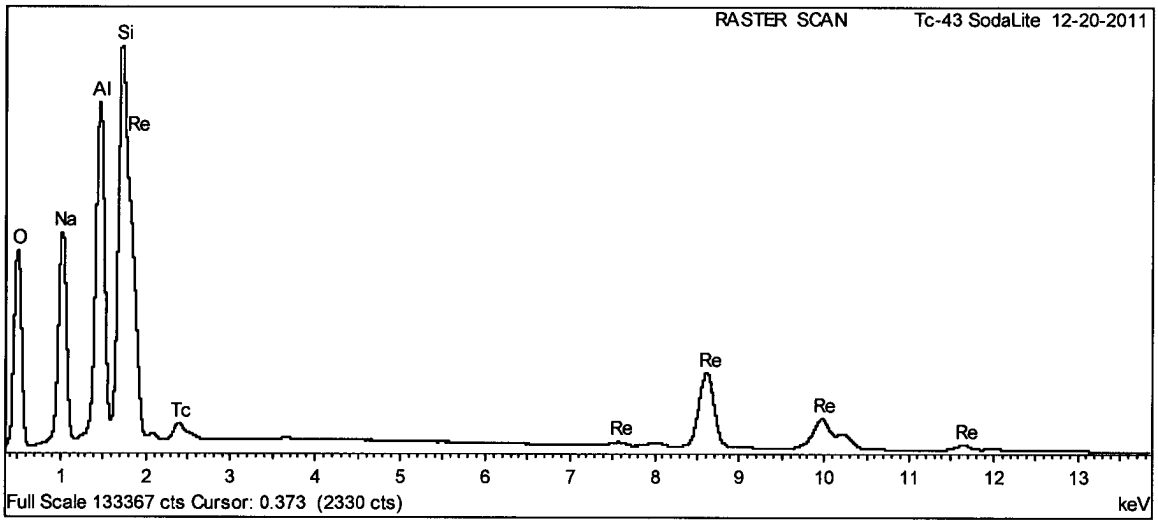

Figure 3-7. SEM-EDS analysis on the Tc-Re Sodalite

Figure 3-8. SEM photograph of the Tc-Re Sodalite

4.0 Conclusions

AD has completed the synthesis of five pure-phase standards - nepheline, nosean, Re-sodalite, Cl-sodalite, and I-sodalite - for the Hanford FBSR program. This particular application is being pursued for the stabilization of LAW in a NAS mineral form. To qualify the waste form, SRNL AD synthesized 200 g of each of the pure-phase standards which will be used for the SPFT testing to determine a forward rate of dissolution and thermodynamic data generation which is needed for a preliminary Performance Assessment (PA). Additional single phase material will be used to develop quantitative XRD calibration curves in the future. X-ray diffraction analysis confirmed that single phases were fabricated, and particle size and surface area measurements for each of the pure-phase standards were determined.

AD was also able to synthesize a mixed sodalite containing rhenium and technetium. X-ray diffraction analysis confirms that a single phase was fabricated, and the Scanning Electron Microscopy with Energy Dispersive X-ray Fluorescence confirms the sodalite contained technetium.

5.0 References

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10. Micromeritics ASAP 2020 Surface Area Analyzer Operator's Manual.

Appendix A – Particle Size Measurements Results

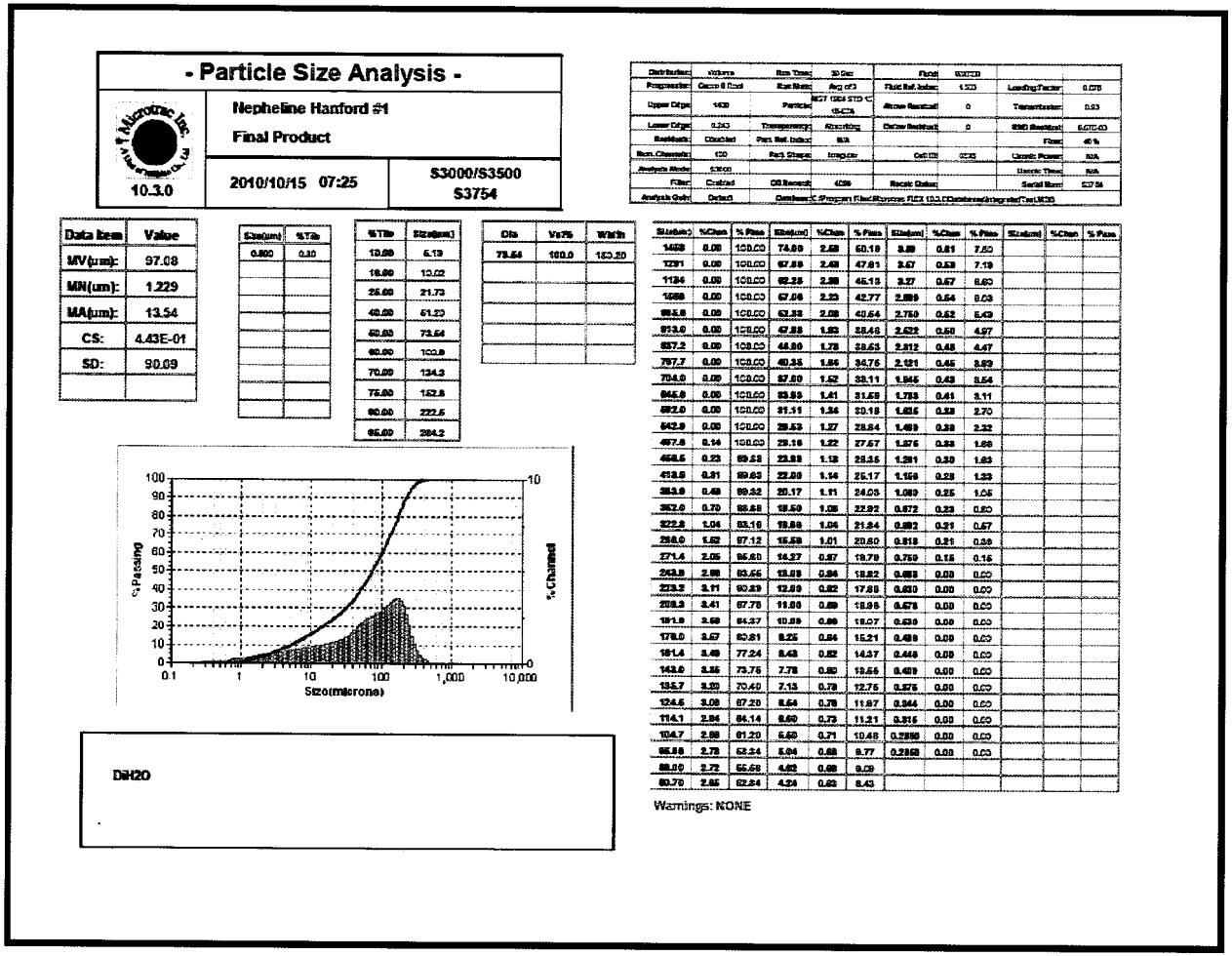

Figure A - 1. Particle Size Measurement Results (Mean Volume Distribution) of the Final Product of Nepheline Sample 1.

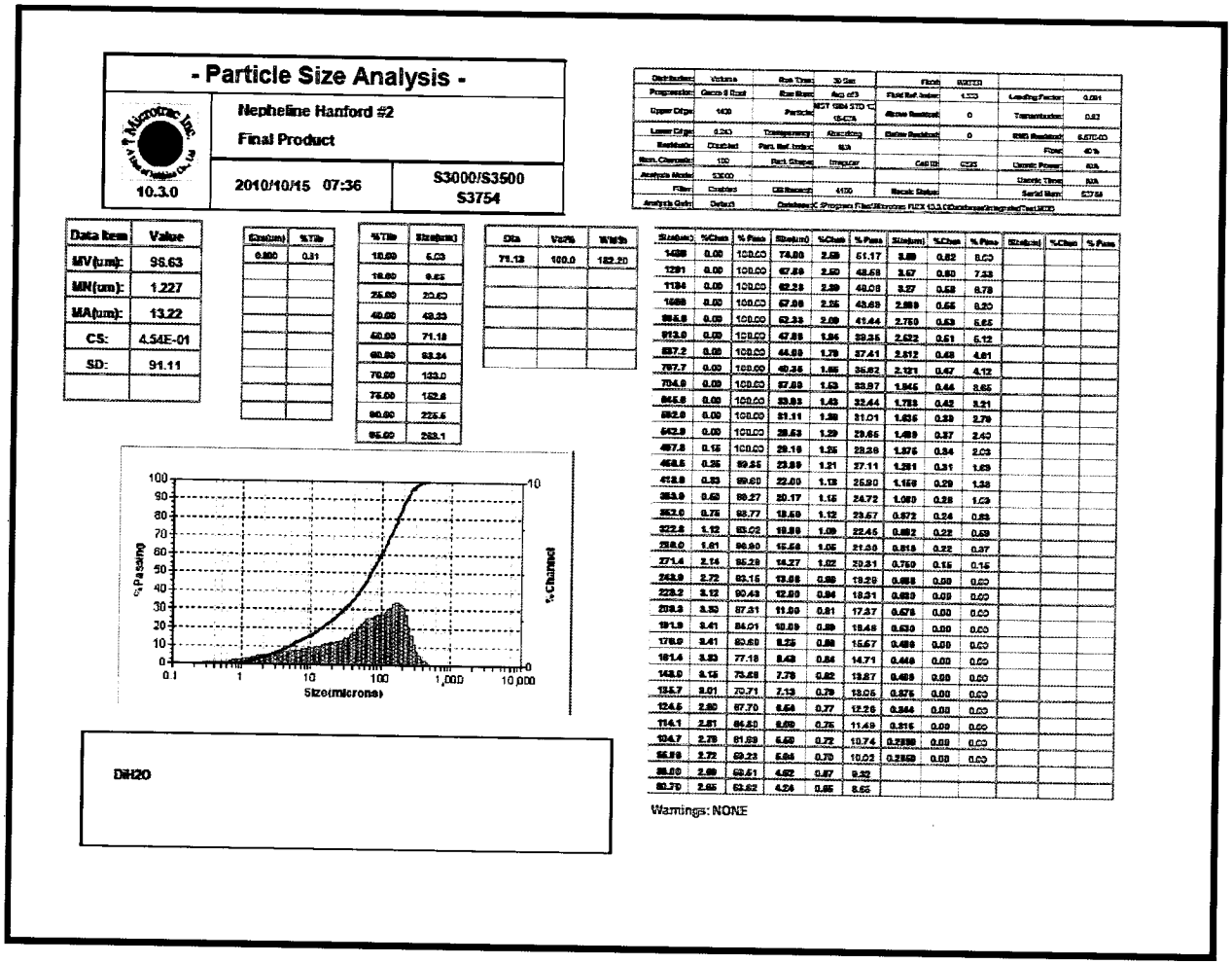

Figure A - 2. Particle Size Measurement Results (Mean Volume Distribution) of the Final Product of Nepheline Sample 2.

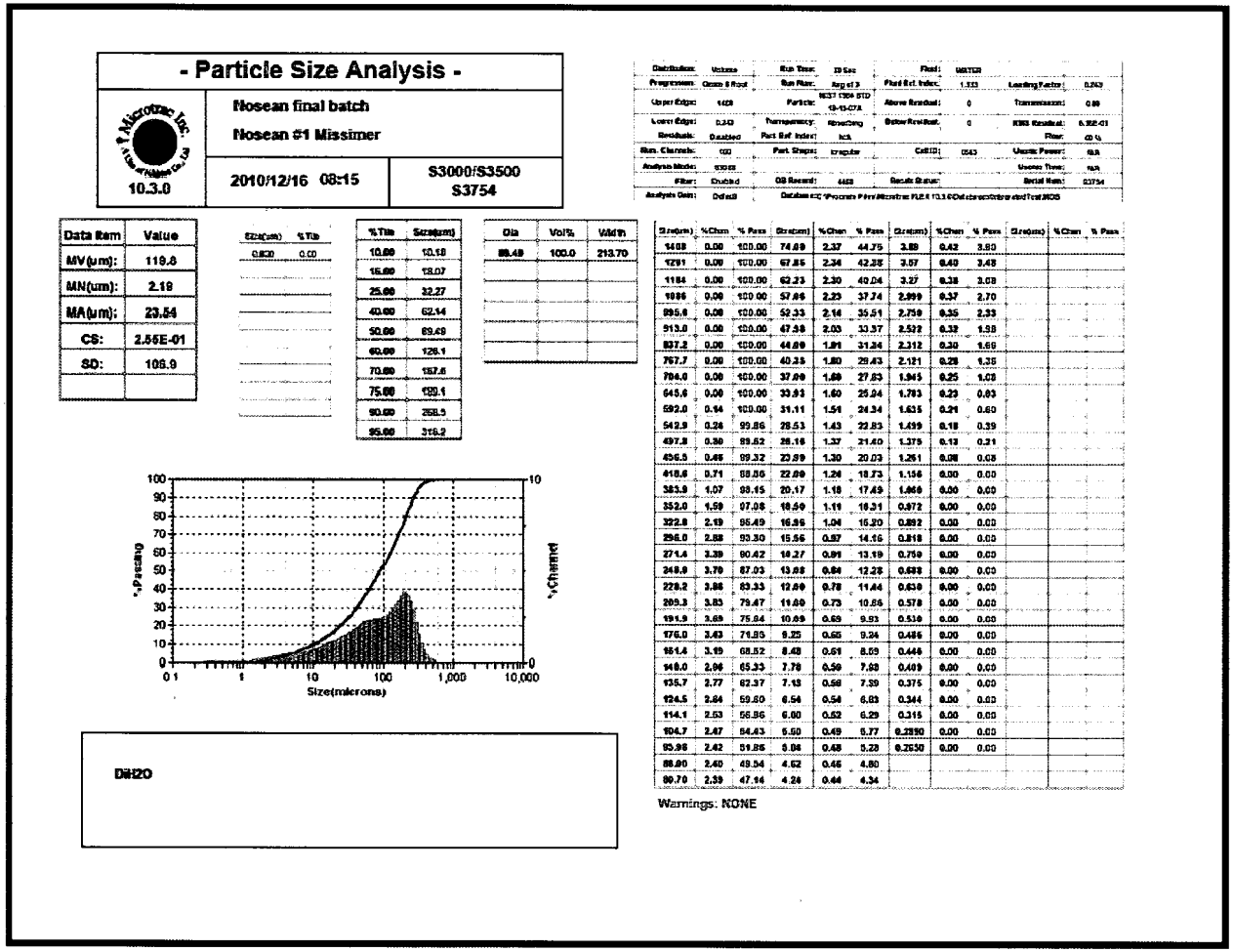

Figure A - 3. Particle Size Measurement Results (Mean Volume Distribution) of the Final Product of Nosean Sample 1.

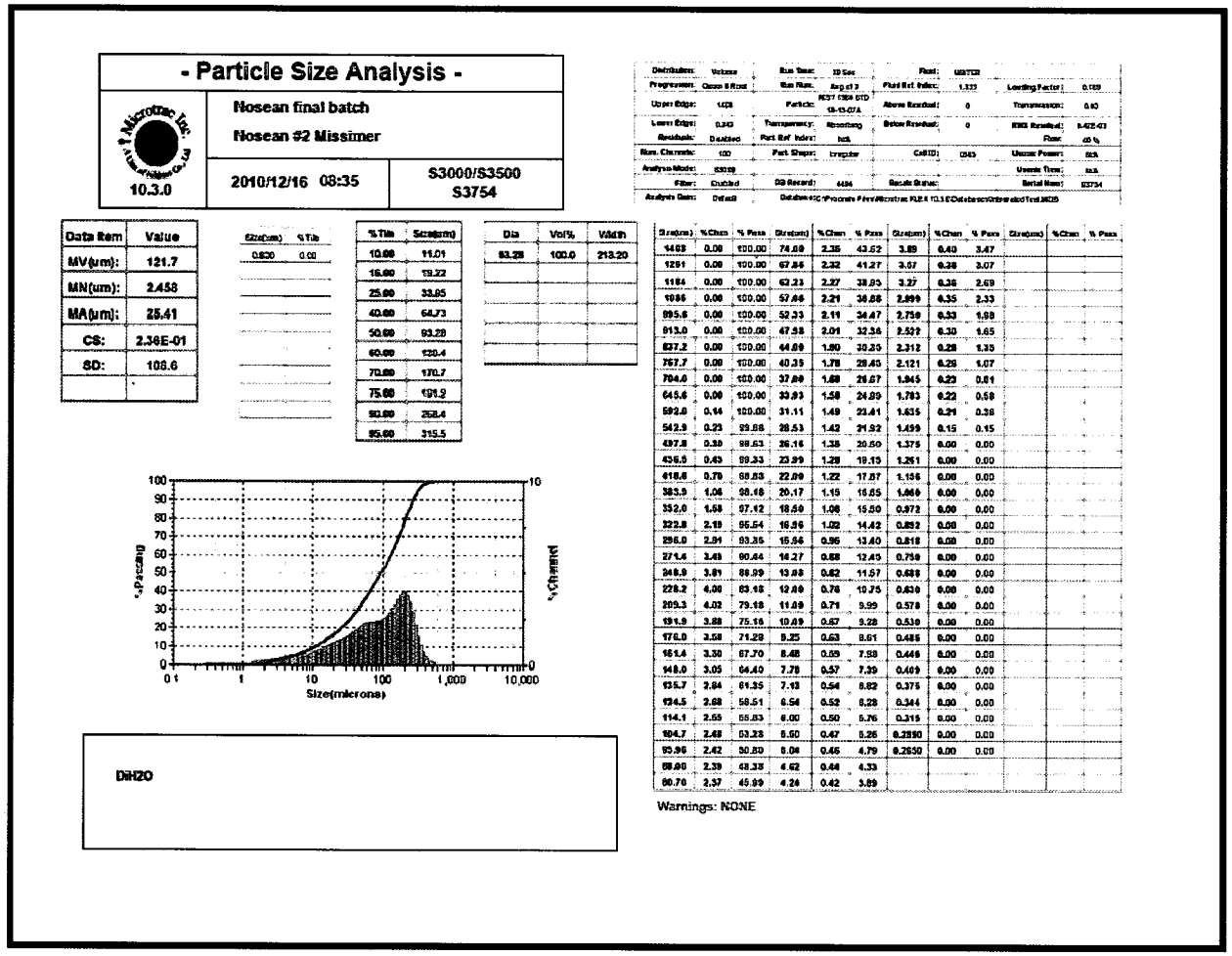

Figure A - 4. Particle Size Measurement Results (Mean Volume Distribution) of the Final Product of Nosean Sample 2.

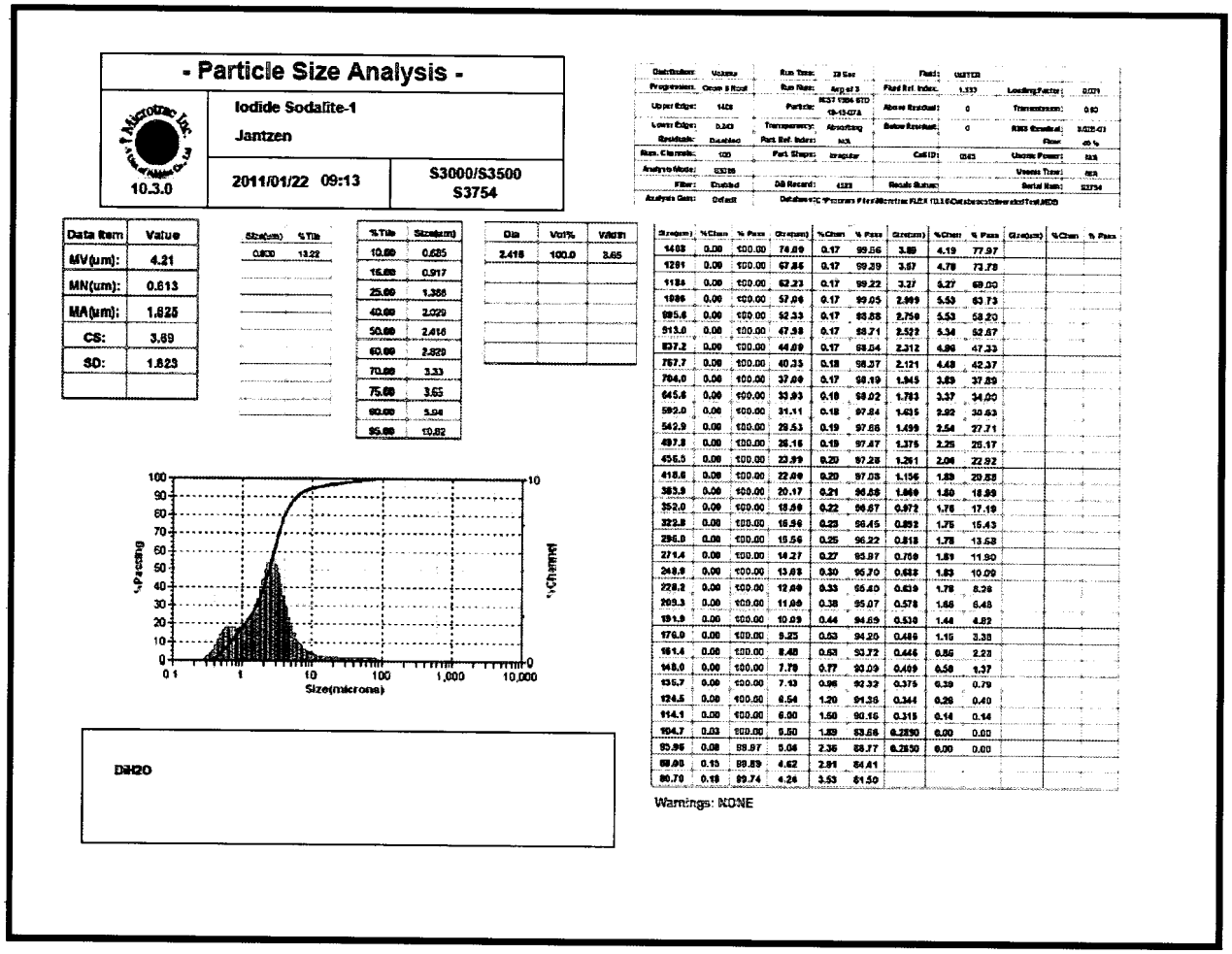

Figure A - 5. Particle Size Measurement Results (Mean Volume Distribution) of the Final Product of I-Sodalite Sample 1.

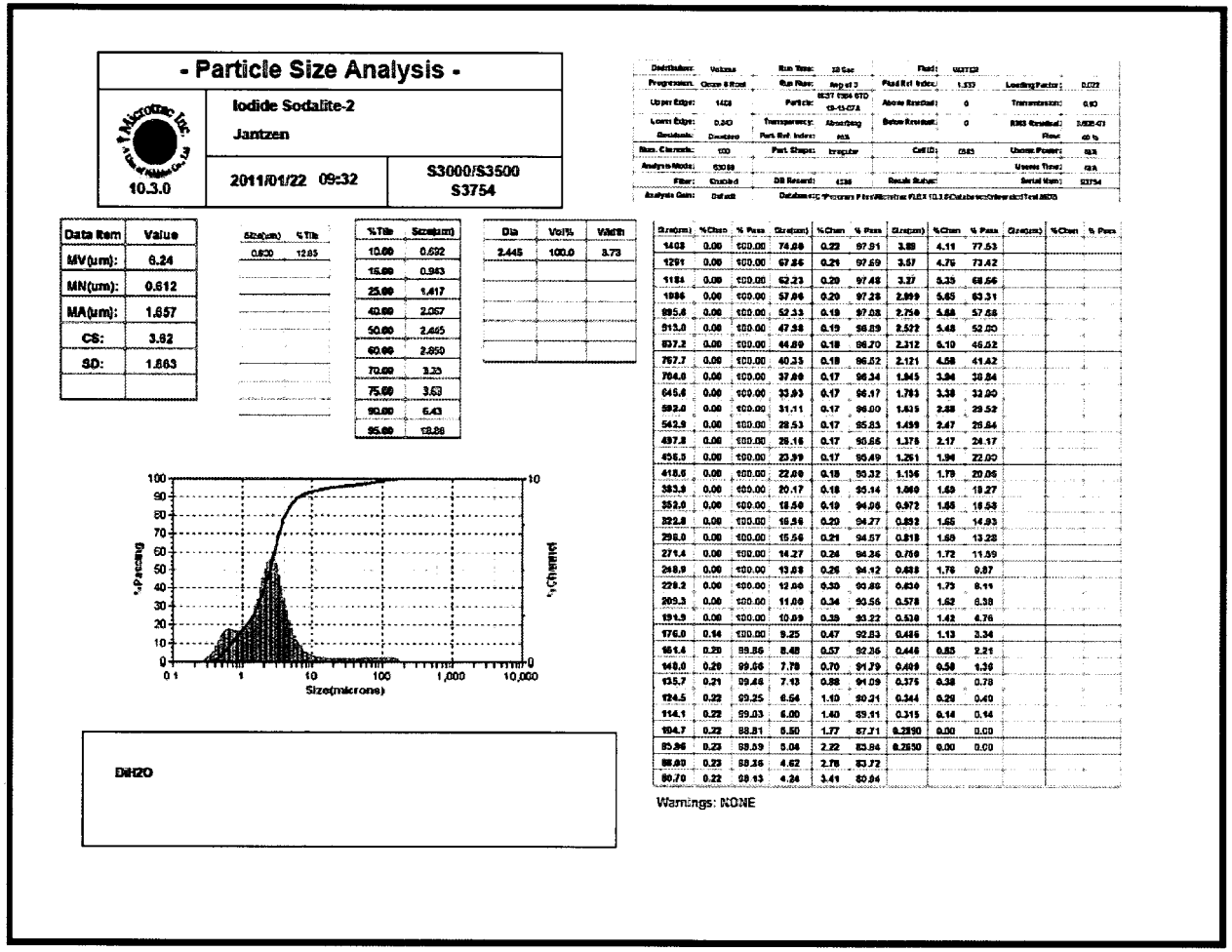

Figure A - 6. Particle Size Measurement Results (Mean Volume Distribution) of the Final Product of I-Sodalite Sample 2.

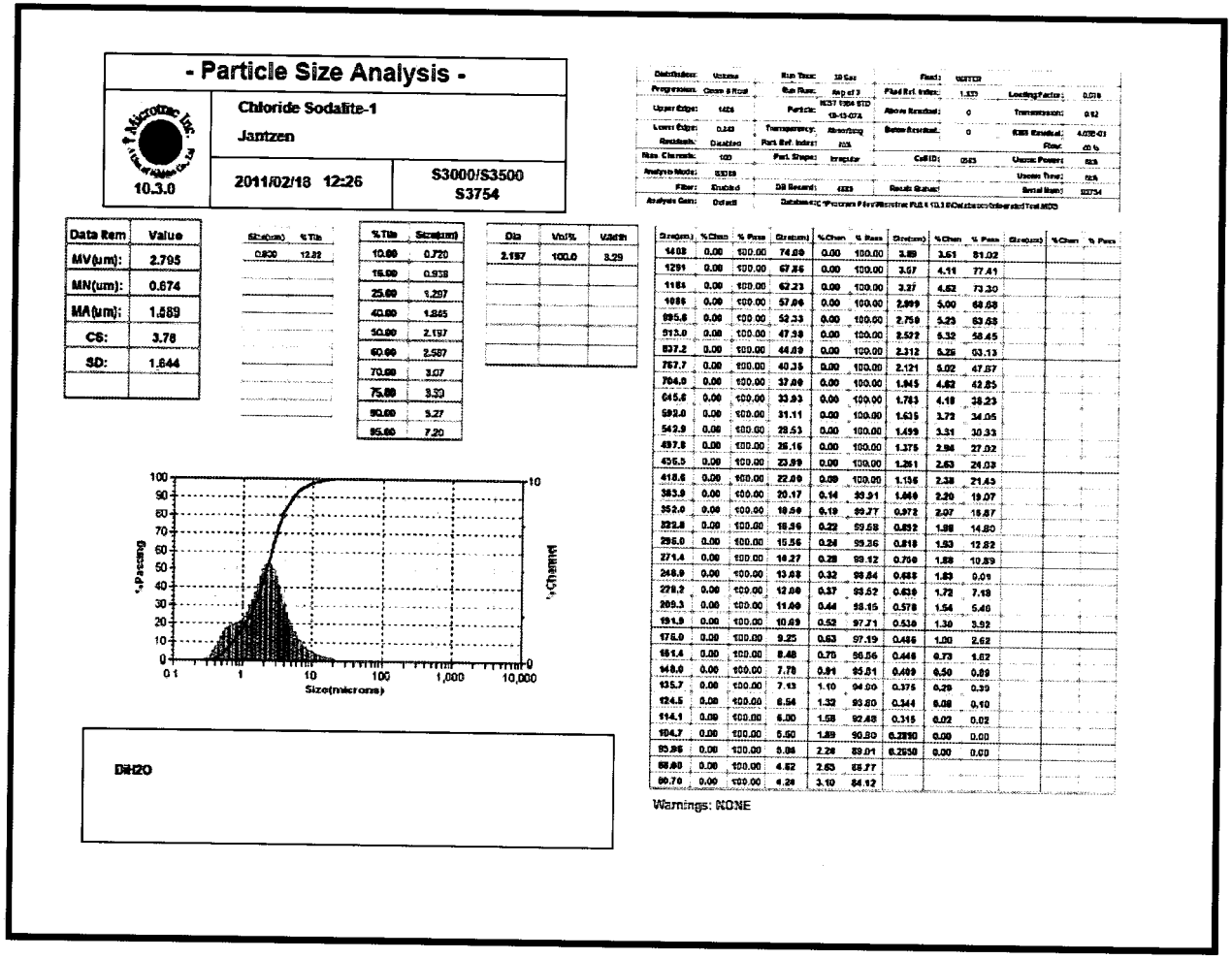

Figure A - 7. Particle Size Measurement Results (Mean Volume Distribution) of the Final Product of Cl-Sodalite Sample 1.

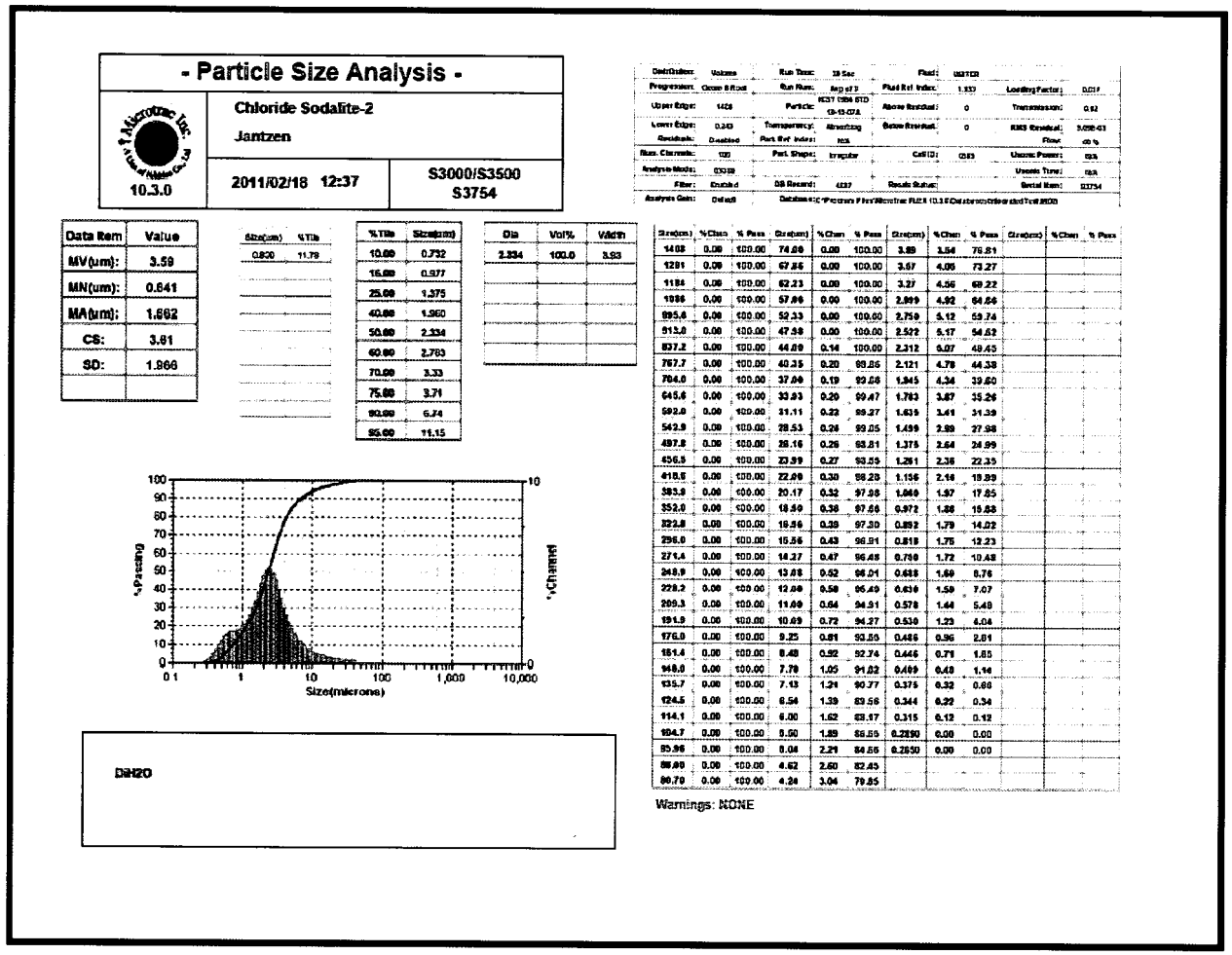

Figure A - 8. Particle Size Measurement Results (Mean Volume Distribution) of the Final Product of Cl-Sodalite Sample 2.

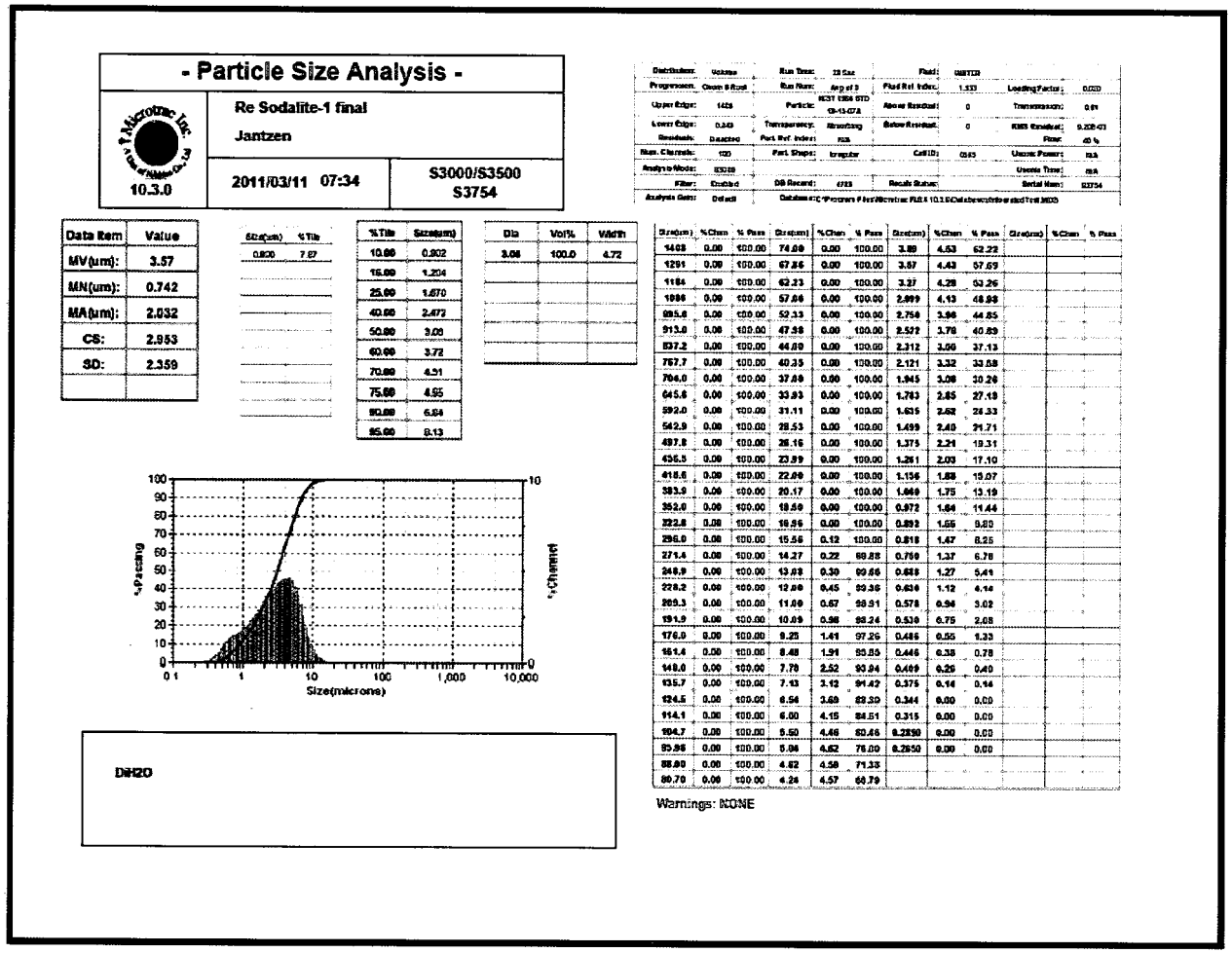

Figure A - 9. Particle Size Measurement Results (Mean Volume Distribution) of the Final Product of Re-Sodalite Sample 1.

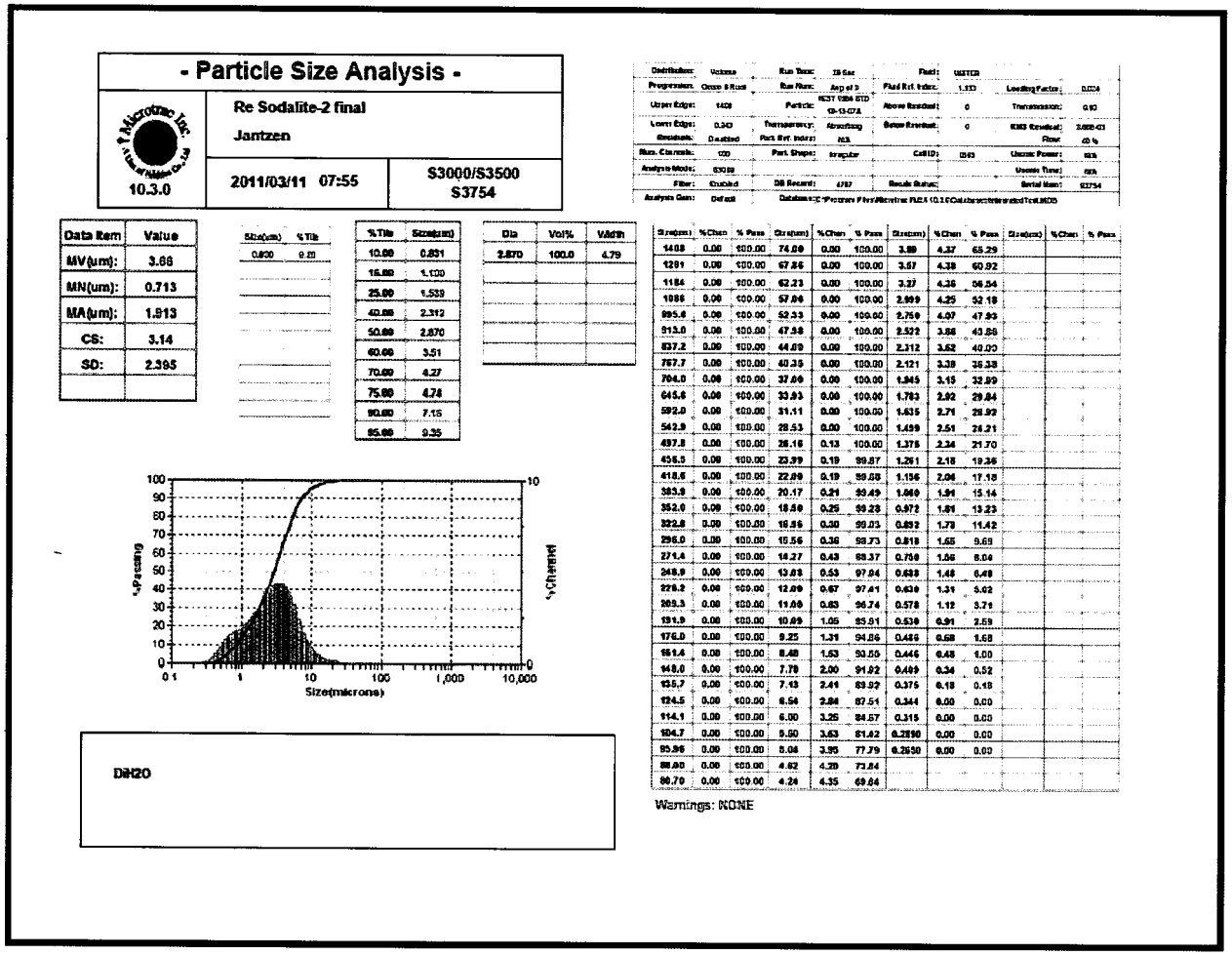

Figure A - 10. Particle Size Measurement Results (Mean Volume Distribution) of the Final Product of Re-Sodalite Sample 2.

Distribution:

C. C. Herman, 773-A
S. L. Marra, 773-A
C. M. Jantzen, 773-A
R. H. Young, 773-A
W. R. Wilmarth, 773-A
C. J. Bannochie, 773-42A
C. L. Crawford, 773-42A
W. E. Daniel, 999-W
P. R. Burket, 773-42A
A. D. Cozzi, 999-W
C. A. Nash, 773-42[a]
D. R. Click, 999-W
D. K. Peeler, 999-W
E. M. Pierce, ORNL
C. F. Brown, PNNL
N. P. Qafoku, PNNL
R. Peterson, PNNL
D. J. Swanberg, WRPS
R. A. Robbins, WRPS