This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available for sale to the public, in paper, from: U.S. Department of Commerce, National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161,
phone: (800) 553-6847,
fax: (703) 605-6900
email: orders@ntis.fedworld.gov
online ordering: http://www.ntis.gov/help/index.asp

Available electronically at http://www.osti.gov/bridge
Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from: U.S. Department of Energy, Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831-0062,
phone: (865)576-8401,
fax: (865)576-5728
email: reports@adonis.osti.gov

This page was intentionally left blank

WSRC-TR-2003-00119, Rev. 0
SRT-RPP-2003-00039, Rev. 0

Key Words:
Evaporation
Submerged Bed Scrubber Recycle

Retention:
Permanent

Key WTP R&T References:
Test Specification: 24590-PTF-TSP-RT-01-009, Rev 0
Test Plan: WSRC-TR-2002-00152
R&T Focus Area: Treated Feed Evaporation
Test Scoping Statement: S94

Treated LAW Feed Evaporation: Physical Properties and Solubility Determination

Jamal E. Josephs, 999-W
Michael E. Stone, 999-W
T. B. Calloway, 999-W
R. E. Eibling, 999-W
C. D. Barnes, 999-W
E. K. Hansen, 999-W

Issue Date: March, 2003

Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

Prepared for the U.S. Department of Energy Under Contract Number DE-AC09-96SR18500

TABLE OF CONTENTS

List of Figures

List of Tables

List of Acronyms

ADS	Analytical Development Section
DOE	Department of Energy
ICP-ES	Inductively Coupled Plasma-Emission Spectroscopy
LAW	Low Activity Waste
NAS	Sodium Aluminosilicate
pAN102	Pretreated AN-102
pAN107	Pretreated AN-107
RPP-WTP	River Protection Project-Waste Treatment Plant
SBS	Submerged Bed Scrubber
SRTC	Savannah River Technology Center
Sr/TRU	Strontium/Transuranic
WSRC	Westinghouse Savannah River Center
XRD	X-Ray Diffraction

List of Figures in Appendix A

1.0 SUMMARY OF TESTING

Evaporation is employed in several places in the Waste Treatment Plant pretreatment process to minimize the volume of waste that must be treated in down-stream vitrification processes. Evaporation is the first unit process in pretreatment (Waste Feed Evaporators), applied before LAW vitrification (Treated Feed Evaporator), and concentrates ion exchange eluate (Cs Eluate Evaporator) prior to HLW vitrification. The goal of the Treated Feed Evaporation process is removal of the maximum water content without producing additional insoluble solids. Prior testing of evaporation systems for process feed was completed to support compliance with regulatory permits and to prepare a model of the evaporation system. These tests also indicated a marked tendency for foaming in the WTP evaporators.[1,2]

To date, evaporation testing and modeling have focused on the Treated feed and Cs eluate evaporation systems.[3,4,5] This has been the first work performed that investigates evaporation of secondary-waste recycle streams in the Treated LAW Feed Evaporator. Secondary-waste recycles from the LAW off-gas scrubbing system have been the major contributors to the overall Treated Feed Evaporator recycle volume. Experience from Savannah River Site operations suggests that the introduction of silica-laden recycles to an evaporator along with high-sodium treated LAW can significantly increase the likelihood of forming sodium-alumina-silicate precipitates upon concentration.[6] Furthermore, there is considerable interest on the part of the WTP project to evaluate the potential of projected evaporator feed and concentrate blends to produce sodium aluminosilicate precipitates.

The work described henceforth is in accordance with RPP Task Specification 24590-PTF-TSP-RT-01-009, scoping statement S94, and *Task Technical and Quality Assurance Plan for Treated LAW Feed: Evaporation and Physical Properties Determination*.[7] This report describes the work the Savannah River Technology Center (SRTC) personnel have performed to determine solubilities of the various simulants of Envelope A, B, and C mixed with simulated River Protection Project Waste Treatment Plant (RPP-WTP) recycle streams. Additionally, as part of this task SRTC personnel have determined various physical properties of the simulant Envelope

---

[1] H. H. Saito, et. al., AN-107 (C) Simulant Bench-Scale LAW Evaporation with Organic Regulatory Analysis WSRC-TR-2000-00486, SRT-RPP-2000-00047, BNF-003-98-0275, Westinghouse Savannah River Company, Aiken, SC, February 2001, p. 9.

[2] Duignan, M. R., "Final Report: Pilot-Scale Cross-Flow Ultrafiltration Test Using a Hanford Site Tank 241-AN-107 Waste Simulant – Envelope C + Entrained Solids + Strontium-Transuranic Precipitation," Savannah River Technology Center, BNF-003-98-0226, March 24, 2000.

[3] A. S. Choi, Estimation of Physical Properties of AN-107 Cesium and Technetium Eluate Blend, SRT-RPP-2000-0061, Westinghouse Savannah River Company, Aiken, SC, February 26, 2001.

[4] T. B. Calloway, Jr., A. S. Choi, P. R. Monson, Evaporation of Hanford Envelope B simulant (AZ-101) Preliminary Report, BNF-003-98-0166, Rev. 1, Westinghouse Savannah River Company, Aiken, SC, January 6, 2000.

[5] W. D. King & T. B. Calloway, Jr., Tank 241-AZ-102 SuperLig® 639 Technetium ion Exchange Eluate Evaporation Study, SRTC-RPP-2000-00024, Rev. 0, Westinghouse Savannah River Company, Aiken, SC, November 30, 2000.

[6] W. R. Wilmarth, et al., Sodium Aluminosilicate Formation in Tank 43H Simulants, WSRC-TR-97-00389 Rev. 0, Westinghouse Savannah River Company, Aiken, SC, November 15, 1997.

[7] T. B. Calloway & M. E. Stone, Task Technical and Quality Assurance Plan for Treated LAW Feed: Evaporation and Physical Properties Determination, WSRC-TR-2002-00152, Westinghouse Savannah River Company, Aiken, SC 29808 (2002).

A, B, and C waste and simulant recycles as a function of sodium concentration and temperature. This information will be used to validate OLI models being developed as part of RPP-WTP test specification "Treated LAW Feed Simulant Evaporation and Physical Property Modeling".[8]

1.1 OBJECTIVES

The overall objectives of the RPP-WTP treated feed program are:

— **Characterize the evaporation of LAW Vitrification plant recycle mixed with treated LAW feed and develop chemical and physical property data for the various mixtures as a function of concentration and temperature**. In these tests, SRTC obtained plant recycles from other R&T subcontractors (e. g., Duratek) and measured a variety of chemical and physical properties (as prescribed by the RPP test specifications) using standard analytical techniques. Chemical and physical analyses such as liquid density, vapor pressure, viscosity, heat capacity, and thermal conductivity of the recycles and blends were conducted before and after evaporation.

— **Develop solubility data for the various evaporation concentrate mixtures and note sodium aluminosilicate formation**. In these tests, SRTC determined the solubility of simulated LAW and recycle blends as a function of temperature and sodium concentration.

— **Evaluate the foaming tendencies of treated LAW feed and recycle simulants under WTP evaporator conditions**. Evaluations of foaming were conducted under this task and any observations were documented for the purpose of foam mitigation studies, using techniques developed under testing prescribed in scoping statements S-118 and S-120.[9]

To achieve these objectives, the RPP-WTP R&T organization via SRTC conducted bench-scale testing with simulants. Experimentation with the most appropriate mixtures from test matrices produced the following data:

- Physical property measurements of density, vapor pressure, viscosity, heat capacity, and thermal conductivity as a function of sodium concentration, weight percent total and insoluble solids, and temperature.
- Measurements of solubility covering the range of expected operating conditions. XRD analysis of simulated LAW and recycle mixtures held over periods of time to determine the potential for formation of sodium aluminosilicate solids.
- Documentation of foaming tendencies of treated feed mixtures of LAW simulants and SBS recycles.

---

[8] R. L. Longwell, Treated LAW Feed: Simulant Evaporation and Physical Properties Modeling, 24590-PTF-TSP-RT-01-008, Bechtel National, Inc., February 2002.

[9] J. E. Josephs and T. B. Calloway, Task Technical and Quality Assurance Plan for – LAW Evaporation: Antifoam/Defoamer testing for Low activity Waste Solutions, WSRC-RP-2001-00791 (SRT-RPP-2001-00142) Rev. 0, Westinghouse Savannah River Company, Aiken, SC 29808, 12/1/01.

1.2 CONDUCT OF TESTING

SRTC facilities and instruments were employed for evaporation studies and density, vapor pressure, and viscosity determination of simulant mixtures. Samples for chemical property characterization were sent to the SRTC Analytical Development Section wherein metal and anion concentrations were measured. ADS also generated XRD plots revealing compositions of solids that precipitated from the mixtures. Solubility data was recorded by using bench-scale evaporation rigs, each capable of pulling an isolated vacuum of over 27 inHg, using diaphragm vacuum pumps. Temperature controlled shaker baths were utilized to provide a medium for mixtures which underwent testing for the presence of sodium aluminosilicates. The foaming tendencies of treated feed simulant mixtures was recorded using simple video and still image devices and other standard methods of measurement.

1.3 RESULTS AND PERFORMANCE AGAINST OBJECTIVES

Small-scale shaker bath and vacuum evaporation studies were conducted using Envelope A, B, and C simulants and simulated plant recycles.[10] Mixtures from all three envelopes were analyzed for density, vapor pressure, viscosity, heat capacity, and thermal conductivity as a function of sodium molarity and temperature. Simulant solubility[11] testing was conducted from a range of 1 M to 10 M sodium and physical properties were also measured as a function of sodium molarity. Volume and weight percent solids were analyzed and the types of solids as a function of sodium molarity were measured by X-ray diffraction. The point of solubility not only defines the upper limit for evaporation, it also defines intermediate points where data should be collected and identifies chemical compounds that have the greatest effect on physical properties. In particular, these evaporation studies address the impact of evaporation of various mixtures to a target sodium molarity defined as 6-8 M Na for Envelope A, 3.5-4 M Na for Envelope B, and 5-6 M Na for Envelope C.

The lowest solubility range for Envelope A was determined 6 to 7 M Na while the highest solubility range for Envelope A mixtures was 7.5 to 8.5 M Na. Total solubility ranges for Envelope B and C mixtures were determined to be between 7 and 8.5 M Na, and 7.5 to 8 M Na, respectively. The most frequent solids identified from XRD analyses were quartz, lithium aluminum carbonate hydroxide hydrate, and sodium nitrate.

The presence of sodium aluminosilicates (NAS) has been noted in various feeds at SRS, thereby suggesting the possibility of their formation in Hanford evaporators. The potential to form sodium aluminosilicates was evaluated during solubility tests. Solids formed during and after evaporation of waste and recycle mixtures were characterized by X-ray diffraction. It was found that a very low frequency of sodium aluminosilicates occurred at 24 hours after the waste simulants and recycles had been mixed. The frequency of NAS was slightly higher in 7-day mixtures and even higher in mixtures that were greater than 7 days old. Since the Treated Feed

---

[10] T. B. Calloway to R. L. Longwell, Interoffice Memo, "Treated Feed Evaporator Preliminary Test Matrix", 6/15/02.

[11] Solubility is the limit (corresponding to sodium concentration) at which a significant amount of additional solids form.

evaporator mean residence time is approximately eight hours, it is not likely that appreciable quantities of sodium aluminosilicates will form inside the evaporator system.

A number of solids unique to Hanford wastes precipitated in the LAW waste simulants and recycle blends. Lithium aluminum carbonate hydroxide hydrate, $(Al_2Li(OH)_6)_2CO_3\ xH_2O$ and Amblygonite, $LiAlF(PO_4)$ were found to precipitate in the majority of the samples testing. Li is added as a glass former and is entrained in the Melter off-gas system and recycled back to the evaporator. Discussions with Hanford personnel indicate that Li will precipitate when combined with Hanford wastes.[12] As previously mentioned, no NAS crystals formed within the evaporator residence time investigated, but other solids did precipitate so scaling inside the evaporator heat exchangers could still be an issue. Several other compounds (ZK-21-$NaAlSiPO_4.xH_2O$, Natrodavyne-$Na_5Al_3CSi_3O_{15}$) containing Si could also present potential problems in the WTP LAW evaporators and will need to be evaluated in the WTP Pilot Evaporator tests and Integrated Pretreatment Pilot tests.

Envelope A, B, and C mixtures exhibited little foaming during evaporation. Any significant foaming occurred only when evaporation was halted, vacuum released (to pull samples), and evaporation restarted. This was, however, only due to inadvertently superheating the warm evaporator contents by suddenly decreasing pressure within the vessel as vacuum was initially applied. Therefore in the plant process, it is recommended that whenever vacuum is released, steam is also temporarily discontinued to prevent superheating conditions.

1.4 QUALITY REQUIREMENTS

This work was conducted in accordance with the RPP-WTP QA requirements specified for work conducted by SRTC as identified in DOE IWO MOSRLE60. SRTC has provided matrices to WTP demonstrating compliance of the SRTC QA program with the requirements specified by WTP. Specific information regarding the compliance of the SRTC QA program with RW-0333P, Revision 10, NQA-1 1989, Part 1, Basic and Supplementary Requirements and NQA-2a 1990, Subpart 2.7 is contained in these matrices.

1.5 ISSUES

Several issues found during testing will need to be addressed by future WTP R&T programs. None of these issues will impact the startup of the WTP, but like the NAS problem found in HLW evaporator system could impact the long term operation of the WTP.

- No NAS crystals formed within the evaporator residence time investigated, but other solids did precipitate so scaling inside the evaporator heat exchangers could still be an issue. Since recycles will be used in the WTP pilot evaporator testing program, scaling will be investigated as a part of that program. If significant scaling occurs, then bench scale scaling and evaporator cleaning studies should be pursued.

---

[12] Reynolds, D. A., email to Calloway T. B., “RE: Double Salt”, CHM2Hill Hanford Group, April 3, 2003. Reyonds, Jacob, email to Reynold, D. A. “When they composite a core sample of AZ101 that was contaminated with Hydrostatic Head fluid, the Li in the sample precipitated when the liquid portion was mixed with the solids portion and then allowed to sit for awhile before analysis (this is documented in the AZ101 Caveat letter). Lithium bromide is used in the sampler hydrostatic head fluid since Hanford wastes contains very little lithium.”

- A number of solids unique to Hanford wastes precipitated in the LAW waste simulant and recycle blends. Lithium aluminum carbonate hydroxide hydrate, $(Al_2Li(OH)_6)_2CO_3.xH_2O$, and Amblygonite, $LiAlF(PO_4)$, were found to precipitate in the majority of the samples testing. Li is added as a glass former and is entrained in the Melter off gas system and recycled back to the evaporator. Lithium aluminum carbonate hydroxide hydrate is not found in the OLI Public database. If the formation of these solids causes undesirable effects in the evaporator system, then modeling and further experimentation to determine the solubility of these compounds should be conducted.

- The presence of NAS was found within a number of Envelope A and C waste feed simulants. This was expected since Si was added to the waste simulants to match the concentration found in Hanford wastes. One-half of Envelope A wastes and one-fourth of Envelope C wastes contained NAS solids suggesting that NAS may be present in stages of the WTP process before the Treated LAW evaporator system. Furthermore, actual analysis of Hanford wastes indicates that NAS solids are present.[13,14,15] Therefore, it would be beneficial to further study possible NAS formation in untreated WTP waste in comparison to pre-evaporator simulated waste and waste blends.

- Since NAS was found to form within a seven day period, the residence time of the WTP process should be evaluated to determine where NAS is likely to precipitate as a crystal. Precipitation within the ion exchange system could be detrimental to the operation of that system. However, if precipitation occurs prior to filtration, the solids would be filtered and sent to HLW vitrification. Since the NAS gel formation kinetics are rapid, the filterability of solutions containing NAS gels should be investigated. An assessment of the filterability of waste feed simulants and recycle solutions is being conducted by the WTP Waste Feed Evaporation R&T task (S-90).

One potential waste recycle stream from LAW vitrification was not investigated by this study. Decontamination solutions containing melter feed or other solutions are currently routed back to the WTP Waste Feed Evaporator system. These solutions should be fairly low in contamination and could be evaporated in the Treated Feed Evaporator. Analysis of the DWPF recycle solutions has shown that approximately 68% of the Si recycled back to the HLW evaporator is due to decontamination streams containing melter feed residues.[16] If future operators of the WTP decide to route decontamination fluids containing Si to the Treated Feed Evaporator, the potential impact of increasing the concentration of Si in the evaporator feed should be evaluated.

2.0 CD-ROM ENCLOSURES

There are no CD-ROM enclosures.

---

[13] Process Aids File 241-105B, Horton, J. E., "Analyses of 105-B Tank", Atlantic Richfield Hanford Company, June 9, 1976.

[14] Process Aids File 241-104AX, Horton, J. E. & Buckingham, J. S., "Characterization and Analysis of 104-AX Sludge", Atlantic Richfield Hanford Company, October 14, 1974.

[15] Process Aids File 241-104A, Horton, J. E. & Buckingham, J. S., "Sluicing and Sludging Achievement Report for Period Ending September 18, 1974", Atlantic Richfield Hanford Company, September 19, 1974.

[16] Lambert, D. P., Barnes, C. D. and Phillips, S. G., "DWPF Recycle Evaporator – Feasibility Study", WSRC-RP-2001-01101 Rev. 0, Westinghouse Savannah River Company, Aiken SC 29808, January 18, 2002.

3.0 METHODS, RESULTS, AND DISCUSSION

3.1 BENCH-SCALE EVAPORATION RIG DESCRIPTION

A diagram of the bench-scale evaporator assembly used in treated feed evaporation studies is shown in Figure 1. The major components of the evaporator assembly were composed of borosilicate glass, Teflon®, and stainless steel. The evaporator vessel, constructed by SRTC glass shop personnel, was made of borosilicate glass with an inner diameter of 3.5 inches and a total volume of 2200 ml. A stainless steel baffle unit was constructed by the SRTC machine shop and was placed inside the evaporator vessel to facilitate thorough mixing, and in turn, decrease bumping tendency of the mixtures. A Fisher 1000-watt IR 4100 infrared hotplate was used to supply adequate heat and stir the mixtures by magnetic coupling of a 1.5 inch, Teflon®-coated magnetic stirbar. A digital Fisher Brand pressure/vacuum gauge was used to monitor the internal pressure of the evaporator system while a Digi-Sense® RTD thermometer monitored the temperature of the mixtures. Vacuum was pulled on the evaporator system by a Vacuubrand MZ 2C diaphragm pump. For this system, the static leak rate criterion of less than 1 inch Hg per 5 minutes was always achieved, corresponding to an air leakage of less than 30 ml/min (at standard temperature and pressure) during evaporations.

3.2 METHODS OF TESTING: INSTRUMENTATION, SOLUBILITY, AND FOAMING

Physical properties (density, vapor pressure, viscosity, and heat capacity) as a function of sodium concentration and temperature were measured for the mixtures and individual streams in order to characterize the evaporation of LAW Vitrification plant Submerged-Bed Scrubber (SBS) recycle mixed with treated LAW feed. For physical properties testing, the simulant mixtures from each envelope identified in the test matrices were concentrated in a Labconco™ RapidVap vacuum evaporator (Figure 2) at 50°C under a vacuum of 27 inches of mercury.

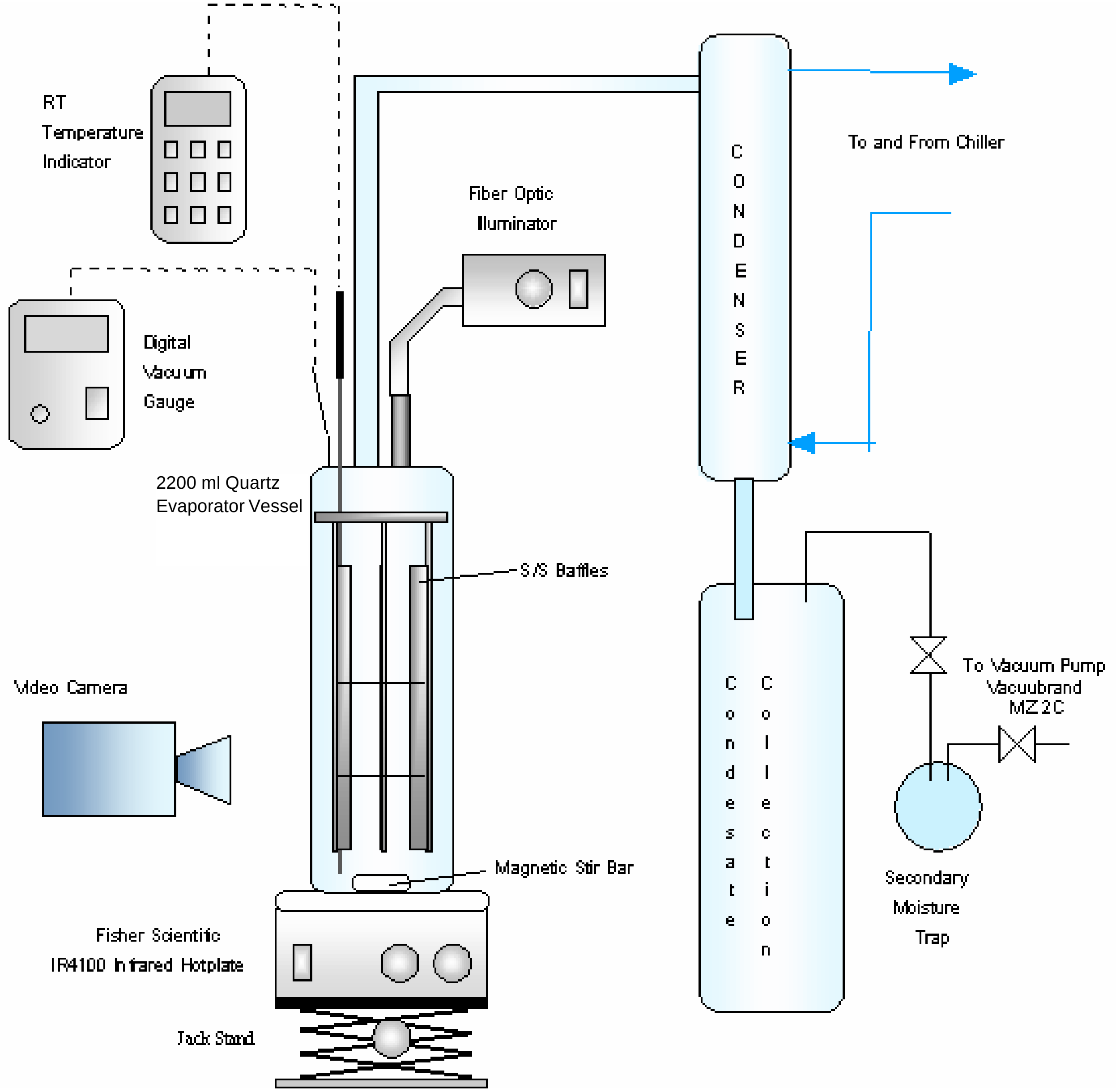

Figure 1. Diagram of Bench Scale Evaporation System

3.2.1 Density, Vapor Pressure, Viscosity, Heat Capacity, and Thermal Conductivity

Initial Envelope A, B, and C waste simulants were thoroughly mixed with the complementary recycles in 1000-ml poly-bottles. The Labconco™ RapidVap vacuum evaporator allowed controlled evaporation of eight beaker solutions total per run since there are eight beaker slots within the instrument. Initial mixtures, approximately 800 ml each, were prepared by mixing the waste simulants with their prescribed recycle counterparts. Then, 50-ml initial samples were removed from each mixture for physical properties testing.

Figure 2. Labconco™ RapidVap Vacuum Evaporator

Approximately half of each remaining mixture was transferred to 500-ml stainless steel beakers, which were used instead of the factory-issued borosilicate glass beakers. Under a vacuum of 27" Hg and fixed temperature of 50°C, the mixtures were then concentrated to Na molarities that were precalculated in relation to the mass and volume of condensate collected. For instance, when the mixtures slightly passed their concentration endpoints, the evaporation process was interrupted and the mixtures were removed from the instrument. Then each mixture was adjusted by mass with its previously evaporated condensate to its appropriate concentration endpoint. After adjustment, while mixing, 30-ml samples were removed from each beaker and placed in labeled 30-ml poly-bottles for physical properties testing. Lastly, each beaker was returned to the RapidVap instrument and evaporation resumed.

Density as a function of temperature and Na concentration was measured by an Anton Paar DMA-4500 Density Analyzer (Figure 3), where density and temperature accuracy = 10^{-3}g/ml and 0.03°C, respectively. Deionized water and 40% sodium nitrate standard solutions were used in calibrating the instrument. Each sample was run twice at 15, 25, 50, and 65°C and the averages of those pairs were reported.

Figure 3. Anton Paar Density Instrument

Figure 4. MiniVap Vapor Pressure Instrument

A MiniVap VOC (Figure 4) from Grabner Instruments, standardized with deionized water, was used to measure **vapor pressure** of the mixtures as a function of temperature. The instrument is preset to read vapor pressures of the samples at 15, 25, 35, 45, 55, and 65°C.

The **rheological properties (viscosity)** were measured using a Haake RS150 rheometer. Since all solutions were suspected to be Newtonian in nature, the viscosity of each solution was measured without performing flow curve measurements. This method can be conducted using a minimal sample volume and sample analysis can be conducted in a fraction of time compared to a complete flow curve. The rheological measurement procedure is summarized below:

1. Select geometry that utilized the minimum amount of sample, but with good response from the Haake RS150.
2. Run random flow curves of actual samples to show that the supernates are indeed Newtonian in nature.
3. Run de-ionized (DI) water flow curves showing there are no secondary flow issues in the shear rate range of measurement. DI water is thinner than any of the supernates, hence secondary flow issues will be seen in the DI water runs. If secondary flow problems are noted, then running the samples in this region of shear rate is avoided.
4. Run random DI water viscosity checks at one shear rate that is within the shear rate run in 3 above. Run at shear rate for 30 seconds and report the average viscosity and temperature between 5 and 25 seconds.
5. Run one shear rate for 30 seconds per sample to obtain viscosity. Report the average viscosity and temperature between 5 and 25 seconds.

The Haake RS150 is a Searle type measuring systems, where both the speed and torque are measured at the rotating shaft. The RS150 rheometer was controlled using a controlled rate. A cone and plate geometry was used to obtain all the flow curves and viscosity data at a specified shear rate. A 60-mm stainless steel measuring plate was installed onto the plate-heating jacket. The 60-mm 0.5 degree angle cone was then installed onto the rotating shaft of the RS150. The RS150, controlled using vendor software/hardware, initially finds the zero point by lowering the cone to the plate, then the cone is raised and a 1-ml sample loaded onto the measuring plate. The cone is then lowered to a predetermined gap setting as determined by the vendor. Excess sample was trimmed from the exposed edge to minimize end effects. The 60-mm, 0.5 degree cone was visually checked to verify that there was no surface damage. The RS150 and 60 mm cone/plate were functionally checked with an S3 oil standard, which was run at least once per day, to verify the operability of the RS150.

A heating/cooling temperature bath was attached to the plate-heating jacket to provide the heat sink. Measurements were taken at 15°C, 25°C, and 60°C. For the 15°C runs, the sample was placed on the plate, the cone lowered, excess removed, and the measurement started when the plate thermocouple measured a temperature of at least 15°C. For the 60°C runs, the cone was preheated to 65°C in a bath, dried, loaded onto the RS150, zero found, sample loaded, cone lowered, excess sample removed, and the measurement taken immediately.

The water results show good agreement with the flow curves and single shear measurements. Typical DI water flow curves and single shear rate measurements are shown in Figures 5 and 6 for 15°C measurements. Flow curves and single shear rate measurements for the actual samples show good agreement. Thus, the method used by SRTC is an acceptable method for characterizing Newtonian fluids, which is the case for LAW pretreated feed material that contains very small solids. This method is recommended for all Newtonian fluids and it is recommended that the rheological section of the RPP-WTP technology development procedure[17] be modified to include this measurement procedure. This methodology was discussed with key WTP personnel (R. L. Longwell, Evaporation Lead and G. Smith, Simulant Validation Lead) prior to performing these measurements.

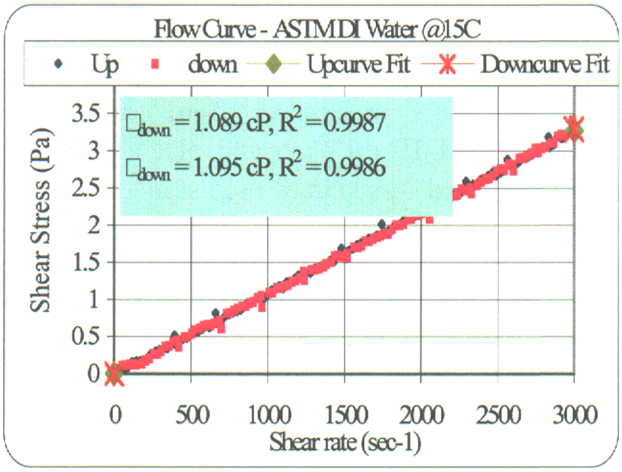

Figure 5. Single Shear Rate Measurement

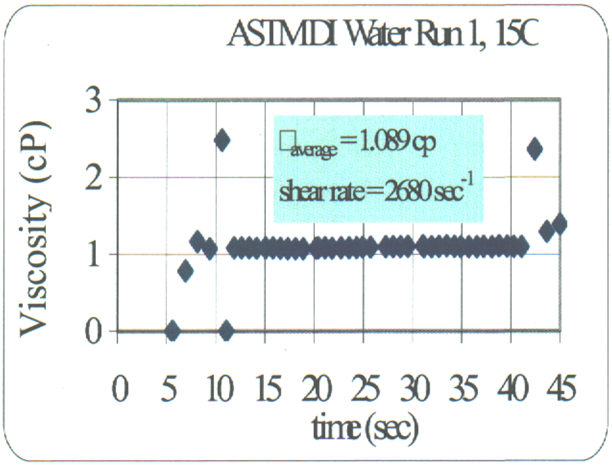

Figure 6. Typical DI H2O Flow Curve

Heat capacity (units of J/g·K) and thermal conductivity (units of W/m·°C) were obtained using a Perkin Elmer DSC 7. The Perkin DSC was calibrated using an Al_2O_3 (aluminum oxide—sapphire) standard from 30 to 85°C and water to measure 1 cal/g·°C.

---

[17] Smith, Gary and Prindiville, Kerry, "Guidelines for Performing Chemical, Physical and Rheological Properties Measurements", 24590-WTP-GPG-RTD-001, Rev. 0, 5/20/02.

3.2.2 Weight and Volume Percent Determination

Weight percent solids was determined using a Mettler/Toledo HR 73 Halogen Moisture Analyzer. Weight % insoluble solids was determined by measuring the solids content of a slurry and subtracting the solids content of supernate filtered from that slurry. When very little solids are present this method can be inaccurate as a result of subtracting two large numbers to obtain a small number. Volume % solids were determined by centrifuging the solids at 4000 rpm and measuring the volume of solids present per total volume of mixture.

3.2.3 Solubility, Solids Characterization, and NAS Formation

The physical properties data regarding the solubilities of mixtures and individual recycle streams of Envelope A, B, and C LAW waste simulants with SBS recycles were measured at 15, 25, and 50°C. The bench scale evaporation rig was employed in solubility studies instead of the RapidVap. Under a vacuum of 27” Hg and temperature range of 46 to 50°C, the mixtures were then concentrated to Na molarities that were precalculated according to the mass of condensate collected. For instance, when a mixture slightly passed its concentration endpoint, the evaporation process was interrupted (heat discontinued and vacuum released) and the condensate was removed from the condensate vessel. By mass, the evaporated mixture was then adjusted with condensate to the precalculated target Na molarity. After adjustment, while mixing, 30-ml samples were removed from the evaporator vessel and placed in labeled 30-ml poly-bottles. Those samples were subdivided into three equal portions of 10 ml each and placed in 15-ml plastic centrifuge tubes. The three equal portions were placed in separate Precision® reciprocal shaker baths at 15, 25, and 50°C and held at temperature for over 12 hours. After the samples were removed from the baths, solids formation was visually noted and weight percent total and insoluble solids were measured with a Mettler/Toledo HR 73 Halogen Moisture Analyzer. The SRTC Analytical Development Section (ADS), using x-ray diffraction (XRD), qualitatively characterized solids. Volume percent solids and weight percent solids at 25°C as a function of sodium molarity were also determined and the results were plotted (see Figure A-40 through Figure A-73 in Appendix A). Samples were also sent to ADS where sodium molarity predictions used in the solubility graphs were confirmed by inductively coupled plasma-emission spectroscopy (ICP-ES) analysis.

The presence of sodium aluminosilicates was studied at 50°C to determine their formation relative to the quantity of time each mixture existed. The waste and recycle streams were mixed and a resulting 16 mixtures were held in 50°C shaker baths for 4, 8, 16, and 24 hr periods. 7-day NAS studies were also performed in which samples were held at 50°C in shaker baths. On the seventh day, samples were removed from the baths, quickly filtered, and their corresponding solids were sent to ADS for XRD analyses.

3.2.4 Foaming

The foaming tendencies of Envelope A, B, and C mixtures were noted during evaporations. Various experimental runs were recorded using a video camera and still images. At an average evaporation rate of 5.5 ml/min[18], foaming tendencies were noted at the very beginning, middle, and end of evaporations. Furthermore, still images were captured of normal boiling and any significant foaming during those intervals.

3.3 MEASURED COMPOSITIONS OF WASTE SIMULANTS AND RECYCLES

Various metal and/or anion concentrations for individual simulants of Envelope A, B, and C are shown in Table 2, 3, and 4, respectively. Metal concentrations of aluminum (Al), sodium (Na), phosphorus (P), sulfur (S), and silicon (Si) were obtained by inductively coupled plasma-emission spectroscopy (ICP-ES) analysis. Anion concentrations were measured by ion chromatography (IC).

3.3.1 Envelope A Waste Simulants

Envelope A waste simulants SM-01, SM-02, SM-03, SM-04, SM-05, SM-06, SM-07, SM-08, SM-09, SM-10, SM-11, and SM-12 were filtered and their supernates were mixed with Duratek LAW SBS condensate. The test matrix for Envelope A LAW was developed previously by Eibling/Edwards for the Waste Feed Evaporation R&T Task S-90 based upon a review of TFCOUP 3A.[19] The matrix is designed to bound the composition of Envelope A wastes expected to be processed by the WTP.[20] The concentrations of Na, Cl, and Si in each of the simulants were to be fixed at 5, 0.102, and 0.00636 mol/L, respectively.[21] The final test matrix was developed using statistical routines available in a commercial software package. Three restrictions were placed on the matrix:

- The solutions must be charge balanced.
- The molar ratio of aluminum to hydroxide must be less than 0.7
- The phosphate and fluoride concentrations must satisfy the following equation:

$$\mathrm{PO_4\,(mol/L)} + 0.07 \cdot \mathrm{F\,(mol/L)} \le 0.05 \tag{1}$$

---

[18] Using an evaporator vessel of area = 53.5 cm^2, the average evaporation (vapor) flux rate was 0.1 ml/min·cm^2, approximately 0.12% design basis flux (~0.87 ml/min·cm^2).

[19] T. B. Edwards, A Statistical Design to support RPP LAW Feed Simulant Testing (U), SRT-GDP-2002-00027, Rev 0, Westinghouse Savannah River Company, Aiken SC, (8/7/02).

[20] The tanks (AP-101, AN104, AN105, SY-101, AN103, AW-101, & AW-104) used to complete this matrix represent the Envelope A waste that will be processed by the WTP to meet the tri-party milestone M-62-00A, "Complete Pretreatment, Processing and Vitrification of Hanford Phase 1 HLW and Low Activity Waste (LAW)," due February 28, 2018.

[21] The design basis density for the Tc Effluent is approximately 1.2 g/ml (≈4.5 M Na). The chloride was fixed to match the average Envelope A concentration and the Si was set to match the maximum Envelope A concentration.

Table 1. Envelope A Simulant Matrix

Test ID	Al mol/L	Cl mol/L	CO_3^{-2} mol/L	F mol/L	NO_2 mol/L	NO_3 mol/L	Na mol/L	OH^- mol/L	PO_4 mol/L	SO_4 mol/L	SiO_3^{-2} mol/L	Oxalate mol/L
SM01	0.71791	0.10200	0.68599	0.00928	0.73098	0.99098	5.00000	1.02559	0.00632	0.00586	0.00636	0.00393
SM02	0.20699	0.10200	0.68599	0.23601	0.73098	1.18854	5.00000	0.98302	0.00632	0.05440	0.00636	0.02001
SM03	0.20699	0.10200	0.42878	0.00928	1.59001	0.99098	5.00000	0.98302	0.04359	0.05440	0.00636	0.00393
SM04	0.20699	0.10200	0.03261	0.23601	0.73098	0.99098	5.00000	2.50293	0.03348	0.00586	0.00636	0.02001
SM05	0.20699	0.10200	0.03261	0.00928	0.73098	0.99098	5.00000	2.74621	0.00632	0.05440	0.00636	0.00393
SM06	0.20699	0.10200	0.36232	0.00928	0.73098	2.08001	5.00000	0.98302	0.04359	0.00586	0.00636	0.00393
SM07	1.12000	0.10200	0.03261	0.00928	0.73098	0.99098	5.00000	1.68923	0.04359	0.05440	0.00636	0.02001
SM08	0.20699	0.10200	0.03261	0.00928	1.59001	1.96007	5.00000	0.98302	0.00632	0.00586	0.00636	0.02001
SM09	0.65443	0.10200	0.03261	0.23601	0.73098	2.08001	5.00000	0.98302	0.00632	0.05440	0.00636	0.00393
SM10	0.80892	0.10200	0.03261	0.23601	1.59001	0.99098	5.00000	1.15560	0.00632	0.00586	0.00636	0.00393
SM11	0.54737	0.10200	0.22536	0.11357	1.00689	1.35628	5.00000	1.24893	0.02627	0.02946	0.00636	0.01189
SM12	0.54737	0.10200	0.22536	0.11357	1.00689	1.35628	5.00000	1.24893	0.02627	0.02946	0.00636	0.01189

Table 2. Measured Metal Concentrations in Envelope A Waste Simulants

Waste Simulant	Al in Waste (mol/L)	Target Al in Waste (mol/L)	% Difference Al Molarity	Na in Waste (mol/L)	Target Na in Waste (mol/L)	% Difference Na Molarity	P in Waste (mol/L)	Target PO4 in Waste (mol/L)	% Difference P Molarity
SM-01	0.859	0.718	20%	5.261	5.000	5%	0.007	0.006	8%
SM-02	0.239	0.207	15%	4.870	5.000	-3%	0.007	0.006	16%
SM-03	0.240	0.207	16%	5.000	5.000	0%	0.055	0.044	26%
SM-04	0.244	0.207	18%	4.826	5.000	-3%	0.012	0.033	-65%
SM-05	0.247	0.207	19%	5.174	5.000	3%	0.007	0.00632	6%
SM-06	0.239	0.207	16%	5.000	5.000	0%	0.045	0.044	4%
SM-07	1.641	1.120	46%	5.391	5.000	8%	0.031	0.044	-28%
SM-08	0.238	0.207	15%	4.957	5.000	-1%	0.007	0.006	12%
SM-09	0.789	0.654	21%	5.087	5.000	2%	0.007	0.006	9%
SM-10	0.963	0.809	19%	5.174	5.000	3%	0.007	0.006	11%
SM-11	0.656	0.547	20%	5.261	5.000	5%	0.014	0.026	-46%
SM-12	0.659	0.547	20%	5.174	5.000	3%	0.015	0.026	-45%

Waste Simulant	Si in Waste (mol/L)	Target SiO3 in Waste (mol/L)	% Difference Si Molarity	S in Waste (mol/L)	Target SO4 in Waste (mol/L)	% Difference S Molarity
SM-01	0.00611	0.00636	-4%	0.00597	0.00586	2%
SM-02	0.00379	0.00636	-40%	0.05688	0.0544	5%
SM-03	0.00414	0.00636	-35%	0.05813	0.0544	7%
SM-04	0.00489	0.00636	-23%	0.00625	0.00586	7%
SM-05	0.00629	0.00636	-1%	0.0575	0.0544	6%
SM-06	0.00411	0.00636	-35%	0.00603	0.00586	3%
SM-07	0.00421	0.00636	-34%	0.05594	0.0544	3%
SM-08	0.00386	0.00636	-39%	0.00634	0.00586	8%
SM-09	0.00507	0.00636	-20%	0.05813	0.0544	7%
SM-10	0.00318	0.00636	-50%	0.00644	0.00586	10%
SM-11	0.00621	0.00636	-2%	0.03156	0.02496	26%
SM-12	0.00607	0.00636	-5%	0.03081	0.02496	23%

3.3.2 Envelope B Waste Simulants

A well-characterized sample of AZ101 was not available for creating a simulant. Therefore, the Best Basis Inventory of 10/1/1998, a mass-based inventory of waste components, was used to develop a composition for AZ101 simulant.[22] The supernate of Tank 241-AZ-101 is not concentrated by processing through an evaporator. As an Envelope B waste, the supernate contains higher ^{137}Cs concentrations than Envelope A. Also, Sr/TRU removal is not required for this waste.

An original radioactive sample of AZ102 concentrated supernate sample had previously been analyzed by SRTC. Characterization data of supernate was used to develop a simulant solution for the AZ102 simulant.[23] Comparison of the data for radioactive AZ102 with the simulant data indicated a good match between most of the analytes in the two systems. This AZ102 recipe was chosen since side by side vitrification testing was conducted using this recipe and actual AZ102 Hanford tank sample. Vitrification testing results indicated this recipe was a valid simulant.

Table 3. Measured Metal/Anion Concentrations in Envelope B Waste Simulants

Component	Measured AZ101 Supernate Conc. (mol/L)	Target AZ101 Supernate Conc. (mol/L)	% Difference AZ101 Supernate Conc.	Component	Measured AZ102 Supernate Conc. (mol/L)	Target AZ102 Supernate Conc. (mol/L)	% Difference AZ102 Supernate Conc.
Metals				Metals			
Al	0.384	0.395	-2.7%	Al	0.004	0.030	-87.8%
Ca	Not Measured			Ca	0.001	0.002	-20.4%
Cr	0.013	0.014	-7.1%	Cr	0.020	0.020	0.2%
K	0.128	0.119	8.1%	K	0.113	0.117	-3.1%
Si	Not Measured			Si	0.002	0.002	14.3%
Na	4.104	4.739	-13.4%	Na	4.449	4.383	1.5%
Non-metals				Non-metals			
F	0.122	0.095	27.4%	F	0.148	0.072	105.0%
NO3	1.269	1.220	4.1%	NO3	0.435	0.440	-1.2%
NO2	1.598	1.414	13.0%	NO2	1.047	1.075	-2.6%

3.3.3 Envelope C Waste Simulants

The tanks within Envelope C are 241-AN-102 and 241-AN-107. Envelope C waste simulants are characterized from Hanford B plant waste that is produced during the Cs/Sr separation and encapsulation processes. Their high organic carbon contents, a result of organic complexing agents and their decomposition products distinguish Envelope C wastes. Due to the complexing agents, concentration of Envelope C wastes requires the removal of increased ^{90}Sr and transuranic (TRU) component concentrations via Sr/TRU precipitation and filtration. The Sr/TRU precipitation procedure was used to pretreat the AN102 simulant.[24] As discussed within that procedure, pretreated AN102 was prepared by using 19 M NaOH, 2 M $Sr(NO_3)_2$, and 1 M $NaMnO_4$ to precipitate strontium and transuranic metals from the solution (Sr/TRU precipitation). The solution was stored for a few days and its filtrate was used in AN102/recycle mixtures.

---

[22] Eibling, R. E. and Nash, C. A., Hanford Waste Simulant Created to Support the Research and Development on the River Protection Project – Waste Treatment Plant. WSRC-TR-2000-00338, Westinghouse Savannah River Company, Aiken, SC 29808, (2000) pp. 26-32.

[23] Crawford, C. L., et. al., Interim Report for Crucible Scale Active Vitrification of Waste Envelope B (AZ-102) (U). WSRC-TR-2001-00395, Westinghouse Savannah River Company, Aiken, SC 29808, (2001).

[24] Bannochie, C. J., Standardized Baseline Precipitation Procedure for Hanford RPP Studies, WSRC-2002-00138, Westinghouse Savannah River Company, Aiken, SC, 29808, (2001).

SRTC Thermal Fluids Laboratory (TFL) had previously pretreated AN107 via Sr/TRU precipitation.[1] The Hanford Tank AN-107 simulant used for this work is a product of the pilot-scale filtration study by Duignan[2] for concentration of precipitated Envelope C waste. At SRTC's Thermal Fluids Laboratory, approximately 100 gallons of Envelope C simulant (AN107) were synthesized. This simulant was a non-toxic version that excluded addition of sodium chromate and lead nitrate. For Sr/TRU removal, the Hanford waste was diluted to 6 M Na before increasing free hydroxide concentration by 0.8 M with 19 M NaOH, strontium concentration by 0.075 M using 1 M $Sr(NO_3)_2$, and manganese concentration by 0.05 M with 1 M $NaMnO_4$. This precipitated AN-107 Envelope C simulant was then cross-flow filtered, producing a filtrate with a measured density of 1.276 g/mL. Dark solids produced by post-filtration precipitation were observed when the filtrate was transferred from the Thermal Fluids Laboratory drum. The filtered supernate of waste simulant Pretreated AN107 was used for Envelope C mixtures. Analytical results for pretreated AN102 and AN107 simulants are reported in Table 4.

On average, comparison of the data for measured cation concentrations with target cation concentrations in Table 2 and Table 3 indicates good matches between most analytes in the systems. Aluminum concentrations were consistently high (average % difference of +20%), for Envelope A waste simulants, but relatively low for Envelope B waste simulants (average % difference of –20%). Sodium and sulfur concentrations were quite close to target concentrations (average % differences of <2% and <9%, respectively) for Envelope A waste simulants. Sodium concentrations were considerably close to target concentrations for Envelope B waste simulants as well (average % difference of ~1%). Low concentration values of elements found in waste simulants suggest precipitation of salts that were subsequently filtered out before sample analysis.

Table 4. Measured Metal/Anion Concentrations in Envelope C Waste Simulants

Component	Measured pAN102 Supernate Conc. (mol/L)	Measured pAN107 Supernate Conc. (mol/L)
Metals		
Al	0.314	0.009
Ca	0.002	0.004
K	0.041	0.047
Na	6.496	5.572
P	0.013	0.009
Si	0.001	0.000
Sr	Not measured	0.873
Non-metals		
Cl	0.085	0.054
F	0.057	0.140
NO3	3.187	2.283
NO2	1.211	0.814
C204	0.012	0.016
PO4	0.020	0.020

3.3.4 Duratek LAW SBS Recycles: Subenvelopes A3, B1, and C2

Off-gas condensates collected from pilot-scale melter runs at Duratek were obtained for analytical testing at SRTC. Condensates were shipped from Duratek in either 55-gallon stainless steel drums or 55-gallon polyurethane drums. Before pulling samples, drum contents were thoroughly mixed with a circulating tube mixer. The LAW recycles used are designated as A3, B1, and C2 according to melter feed formulations processed by the Duratek LAW melter. The A3, B1, and C2 designations refer to the glass formulation for subenvelopes A3, B1, and C2 as categorized in Table 5. The percent and type of recycle in Envelope A, B, and C mixtures are listed in Table 6.

Table 5. LAW Tank Categories

Current Envelope Designation	Envelope A			Envelope B		Envelope C	
Sub-Envelope	A1	A2	A3	B1	B2	C1	C2
Tanks applicable to this subset	AN-105 SY-101 AN-103	AP-101 AW-101	AN-104 possibly AP-108	Blended AZ 101 & AZ-102	AZ-102	AN-107	AN-102 possibly S-102
Na2O wt%	20.0%		14.8%	6.5%	5.0%	~14%	11.2%
K2O wt%	0.3 - 0.7%	~2%	~0.3%	~0.2%	~0.2%	~0.3%	~0.2%
SO3 wt%	0.1 - 0.2%	0.1 - 0.2%	~0.35%	0.75%	~1%	~0.35%	~0.45%
Formulation Selected	LAWA44	LAWA88	LAWA102	LAWB45	LAWB53	LAWC22	LAWC21

Table 6. Treated Feed Envelope A, B, C Mixture Ratios

Hanford Waste Envelope	Waste Simulant	SBS Recycle	Initial Na Conc. (M) of Blended Evaporator Feed[25]	Percent Recycle (%)
A[26]	SM-01 – SM-12	Duratek **A3** LAW SBS	2	55
	AP101	Duratek **A3** LAW SBS	2	55
B	AZ101 Supernate	Duratek **B1** LAW SBS	1.2	70
	AZ101 Supernate	Duratek **B1** LAW SBS	1.3	60
	AZ102 Supernate	Duratek **B1** LAW SBS	1.7	70
	AZ102 Supernate	Duratek **B1** LAW SBS	1.8	60
C	Pretreated AN102	Duratek **C2** LAW SBS	2	55
	Pretreated AN102	Duratek **C2** LAW SBS	2	43
	Pretreated AN107	Duratek **C2** LAW SBS	2	55
	Pretreated AN107	Duratek **C2** LAW SBS	2	43

Table 7 and Table 8 present measured physical and chemical property data, respectively, for each recycle utilized. With very low total and insoluble solids contents, the Duratek subenvelopes A3, B1, and C2 LAW SBS recycles had densities that were virtually identical to that of water. Duratek C2 recycle had the highest sodium content followed by Duratek A3 recycle. Lithium solids found in XRD analyses are due to lithium from all three recycles, with the highest concentration of lithium from C2 recycle.

---

[25] Target values.

[26] Preliminary testing with Envelope A mixtures demonstrated that differences between mixtures of 55% and 43% SBS recycle were insignificant, so 43% recycle mixtures were not further tested.

Table 7. Physical Properties of Duratek LAW SBS Recycles

Physical Properties	A3	B1	C2
pH Before Mixing	6.9	7.6	6.9
Density (g/ml)	1.02	1.00	1.03
Wt. % Insoluble Solids	0.032%	0.11%	0.15%
Wt. % Total Solids	0.84%	0.46%	1.61%

Table 8. Metals Analysis of Duratek Subenvelope A3, B1, and C2 LAW SBS Recycles

		A3		B1		C2
Metals		(mol/L)		(mol/L)		(mol/L)
Al		0.000825		0.000136		0.006375
B		0.068680		0.025900		0.111923
Ba	<	0.000002	<	0.000000		0.000011
Ca		0.001759		0.000075		0.014945
Cd	<	0.000012	<	0.000000	<	0.000002
Co	<	0.000004	<	0.000001	<	0.000014
Cr		0.000210		0.000040		0.001415
Cu	<	0.000003		0.000007		0.000017
Fe		0.000381		0.000011		0.002892
K		0.005626		0.000527		0.008312
La	<	0.000002	<	0.000010	<	0.000072
Li		0.006730		0.003790		0.022770
Mg		0.000481		0.000197		0.003393
Mn	<	0.000001		0.000001		0.000032
Mo	<	0.000004		0.000004		0.000046
Na		0.068944		0.006612		0.204873
Ni	<	0.000006		0.000016		0.000332
P		0.000050	<	0.000044	<	0.000484
Pb	<	0.000002	<	0.000007	<	0.000072
Re		NA	<	0.000001	<	0.000011
S		0.010931		0.027352		0.068925
Si		0.003513		0.001050		0.025179
Sn	<	0.000024	<	0.000004	<	0.000032
Sr	<	0.000001		0.000000		0.000018
Ti		0.000139		0.000010		0.001127
V	<	0.000049	<	0.000005	<	0.000059
Zn		0.000503		0.000454		0.004130
Zr		0.000014		0.000007		0.000241

3.4 MEASURED COMPOSITIONS OF MIXTURES: WASTE SIMULANTS + RECYCLES

Essentially three general experimental studies were performed concerning LAW Vitrification waste simulants and recycle stream mixtures: (1) characterize the evaporation of LAW Vitrification plant recycle mixed with treated LAW feed and develop chemical and physical property data for the various mixtures as a function of sodium concentration and temperature; (2) develop solubility data for the various evaporation concentrate mixtures and note sodium aluminosilicate formation; and (3) evaluate the foaming tendencies of treated LAW feed and recycle simulants under WTP evaporator conditions.

Table 9 and Table 10 display data of Envelope A, B, and C mixtures at the percentages presented in Table 6. Note that, on an average, the target concentration of Na in Envelope A mixtures did not stray more than ±10% from the actual mixtures' Na concentrations. Thus, full chemical analyses of Envelope B and C mixtures used in these tests were not conducted. Sodium analysis was completed for Envelope A, B, and C mixtures and concentrates to confirm predicted concentration and dilutions.

Table 9. Al, Na, S, P, Si Concentrations in Initial Envelope A Mixtures (55% Recycle)

Waste Simulant	Target Na M in Mixture	Measured Na M in Mixture	% Difference Na M	Target P M in Mixture	Target Si M in Mixture	Target S M in Mixture	Target Al M in Mixture
SM-55-01	2.15	2.01	-6.3%	0.0028	0.0025	0.0024	0.3504
SM-55-02	1.97	2.10	6.7%	0.0030	0.0015	0.0230	0.0966
SM-55-03	2.02	-----	-----	0.0222	0.0017	0.0235	0.0970
SM-55-04	1.94	2.20	13.5%	0.0047	0.0020	0.0025	0.0982
SM-55-05	2.08	-----	-----	0.0027	0.0025	0.0231	0.0993
SM-55-06	2.03	2.18	7.6%	0.0184	0.0017	0.0024	0.0970
SM-55-07	2.21	2.18	-1.2%	0.0128	0.0017	0.0229	0.6715
SM-55-08	2.00	2.16	7.8%	0.0029	0.0016	0.0026	0.0961
SM-55-09	2.07	2.13	2.9%	0.0028	0.0021	0.0237	0.3212
SM-55-10	2.10	2.13	1.3%	0.0028	0.0013	0.0026	0.3913
SM-55-11	2.14	2.25	5.4%	0.0057	0.0025	0.0128	0.2661
SM-55-12	2.10	2.24	6.7%	0.0059	0.0025	0.0125	0.2676

Table 10. Na Concentrations in Initial Envelope B and C Mixtures

Waste Envelope	Waste Simulant	% Waste (%/100)	Measured Na M in Mixture	% Recycle (%/100)	Target Mixture Na M	% Difference Na M
B	AZ101-SUP	0.3	1.22	0.7	1.2	1.3%
	AZ102-SUP	0.3	1.16	0.7	1.3	-10.5%
	AZ101-SUP	0.4	1.62	0.6	1.2	35.3%
	AZ102-SUP	0.4	1.55	0.6	1.3	19.5%
C	pAN102	0.45	2.10	0.55	2	4.9%
	pAN107	0.45	2.94	0.55	2.72	8.2%
	pAN102	0.45	2.16	0.55	2	8.0%
	pAN107	0.45	3.03	0.55	2.72	11.3%

3.5 DISCUSSION OF CHEMICAL AND PHYSICAL PROPERTY DATA

Envelope A, B, and C waste simulants, RPP-WTP SBS recycle simulants, and their respective mixtures were jointly characterized by the Immobilization Technology Section (ITS) and ADS. Physical property data including density, vapor pressure, viscosity, heat capacity, and thermal conductivity are plotted in the graphs in Appendix A.

3.5.1 Density

Represented in Figure 7 are general density trends formed by Envelope A, B, and C mixtures at 25°C. There exists a characteristic increase in density as the concentration of sodium increases in each envelope. Therefore, sodium concentration has a significant impact on density. Envelope C mixtures have the highest density trend with a slightly steeper slope (0.0479) than Envelope A and B mixtures. Envelope A and B mixtures have nearly identical density trends with similar slopes (0.0386, 0.0402, respectively).

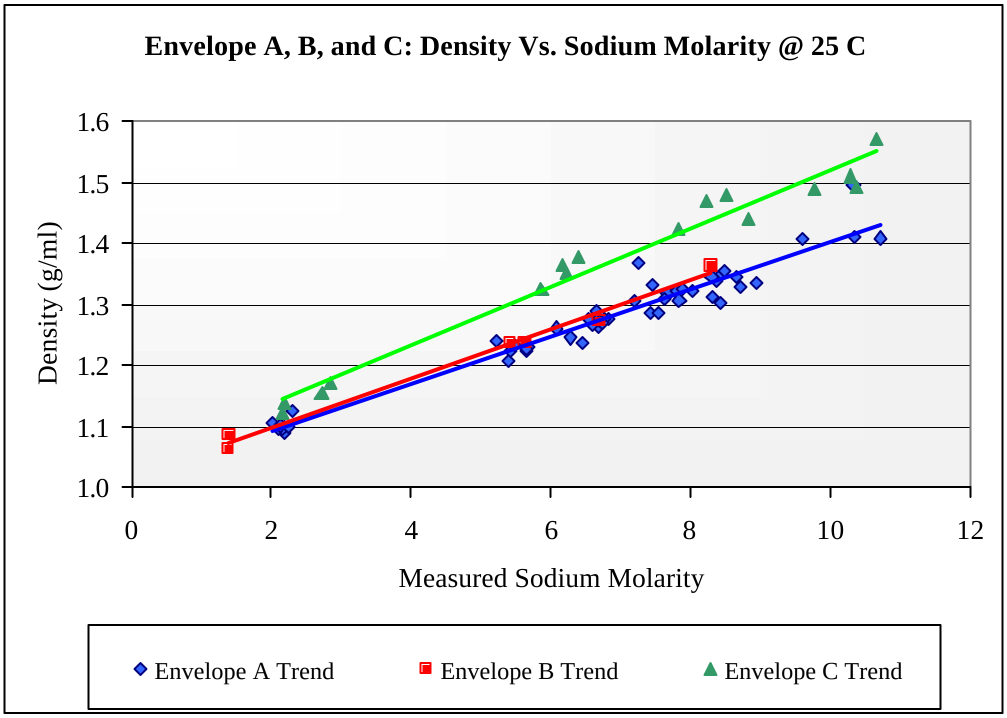

Figure 7. General Trends of Envelopes A, B, and C Densities Vs. Sodium Molarity

In Appendix A, Figure A-1 through Figure A-8 present densities of Envelope A, B, and C mixtures at 15, 25, 50, and 65°C. As a function of temperature, densities of all three waste envelopes decrease as temperature increases. Preliminary testing with Envelope A mixtures demonstrated that physical characteristic differences between mixtures of 55% and 43% recycle were insignificant, so 43% recycle mixtures were not tested. For Envelope B (70% and 60% recycle) and C (55% and 43% recycle), densities of the mixtures had little variance, such that it is concluded that the mixture ratios have very little affect on the densities of the mixtures. Additionally, variances in density as a function of temperature was quite low (≤ 5% difference).

3.5.1.1 Empirically Derived Formulas

Based on observations, a set of empirically derived formulas for densities, vapor pressures, and viscosities as a function of sodium molarity was generated to show trends of Envelope A, B, and C mixtures. For example, as presented in Figure 8, based on measured data, the empirical formula

$$y = (a + bx)^2 \quad (2)$$

(where **y** equals density, **a** and **b** equal the fitting parameters[27] of the given equation, and **x** equals Na molarity) resulted a best fit for densities of Envelope A mixtures at 25°C.[28] The single white (innermost) line on the graph in Figure 8 is the curve fit based on the empirical formulas. The two red lines directly outside of the single white line represent 95% confidence intervals in which a Y-value range (for any given X value) has a 95% probability of containing the true corresponding Y value. In other words, the tighter the red lines are about the white line, the better the formula represents the data trend. Moreover, tighter confidence levels suggest that measured data on the trend is consistent. The looser the red lines are about the white line, the worse the formula represents the data trend. The two outermost green lines represent 95% prediction intervals wherein based on the actual data there is a 95% probability that future measurements would yield data within that range. Hence, prediction intervals suggest a range around the curve fit in which future data would possibly lie. Empirical formulas derived for densities, vapor pressures, and viscosity are chosen in accordance with 5 main criteria:

- The overall population of points directly on the curve fit
- How well the empirical formula fits published H_2O data
- The tightness of 95% confidence and prediction intervals
- R^2 values closest to 1.0
- How natural or smooth the curve visually appears.

The remaining graphs with the corresponding empirical formulas for density, vapor pressure, and viscosity are located in Appendix A, Figure A-29 through Figure A-36. Empirically derived formulas and fitting parameters for densities of Envelope A, B, and C are listed in Table 11.

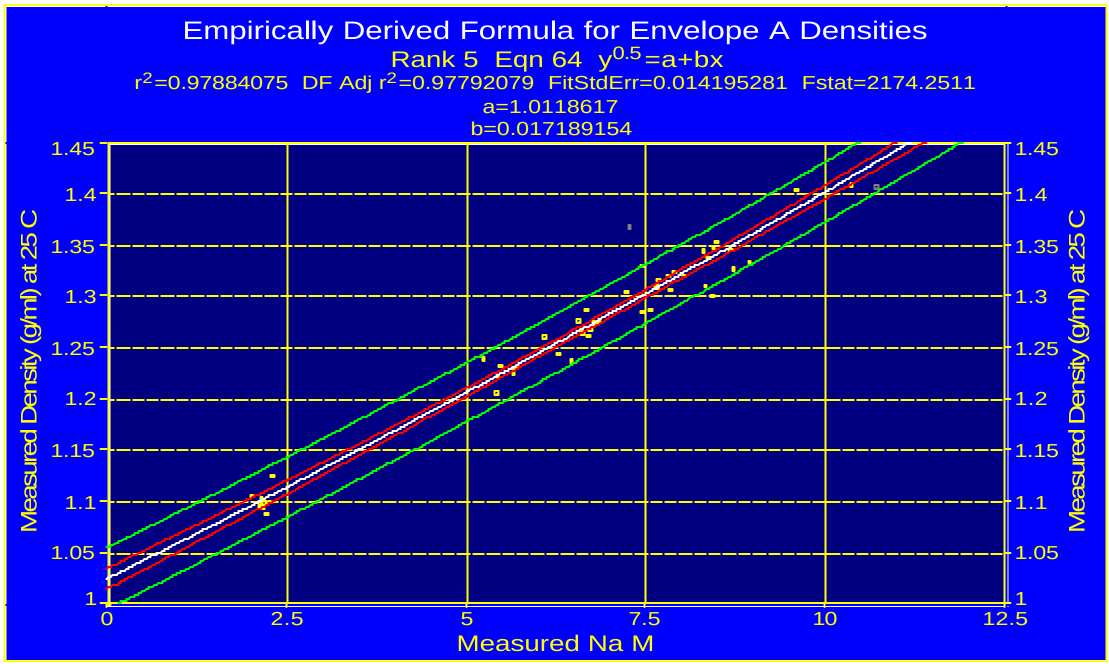

Figure 8. Empirical Formula for Envelope A Density Trend

---

[27] Shown in the heading area of each graph.

[28] The value for water at 25°C is plotted in all empirical formula charts for a reference point of known physical property behavior and for comparison to simulant data.

Table 11. Emperically Derived Formulas of Densities

Waste Envelope Mixtures	Formula	Fitting Parameter **a**	Fitting Parameter **b**	R^2
Envelope A	$y = (a + bx)^2$	1.0118617	0.017189154	0.97884075
Envelope B	y = 1/(a + bx)	0.97874773	-0.029760383	0.98946044
Envelope C	y = a·exp(-x/b)	1.0471278	-25.925581	0.97306981

3.5.2 Vapor Pressure

Figure 9 illustrates the general vapor pressure trends of Envelope A, B, and C at 25°C. A typical decrease in vapor pressure as sodium molarity increases is observed with Envelope A and C mixtures having nearly identical trends and slopes (-1.082 and -1.089, respectively). Over a sodium molarity range from about 1.5 M to 11 M, vapor pressures decrease over a range of nearly 13 mmHg. The effect of sodium on vapor pressure is indeed significant. Comparatively, the Envelope B trend is in the same range as Envelope A and C trends. In Appendix A, Figure A-9 through Figure A-16 illustrate vapor pressures of Envelope A, B, and C mixtures at 15, 25, 35, 45, 55, and 65°C. As a function of temperature, vapor pressures of all three waste envelopes increase parabolically as temperature increases.

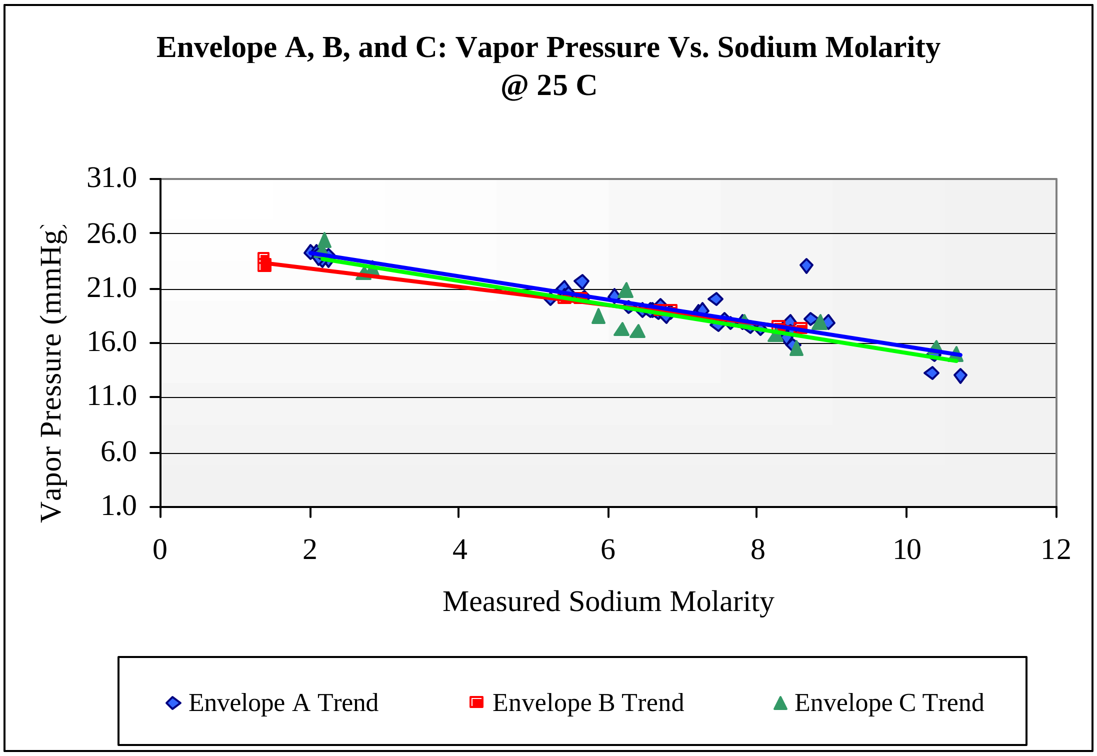

Figure 9. General Trends of Envelope A, B, and C Vapor Pressures Vs. Sodium Molarity

For Envelope A, B, and C, vapor pressures of all the different recycle mixture ratios had no significant variance from initial mixtures, thus demonstrating that mixture ratios had little affect on vapor pressure. However, temperature and sodium molarity had a noticeable affect on vapor pressure. It is observed that there is a progressively larger spread in vapor pressures at higher temperatures as Na molarity increases. For example, for 2 molar Na mixtures, vapor pressures are virtually superimposed throughout the entire range of 15°C to 65°C. However, for 6 molar mixtures, as temperature increases, vapor pressures begin to spread apart with the largest spread at 65°C. Consequently, an even larger variance is observed in 8 molar mixtures at the higher range of 65°C (see Figure A-9 through Figure A-12 for example). Empirically derived formulas and fitting parameters for vapor pressures of Envelope A, B, and C are listed in Table 12.

Table 12. Emperically Derived Formulas of Vapor Pressures

Waste Envelope Mixtures	Formula	Fitting Parameter **a**	Fitting Parameter **b**	R^2
Envelope A	y = 1/(a + bx)	0.035902066	0.0024934388	0.94836656
Envelope B	y = 1/(a + bx)	0.037033834	0.0024360036	0.94145987
Envelope C	y = 1/(a + bx)	0.035075273	0.0028362417	0.9279379

For Envelopes A, B, and C, the average temperature at which the vapor pressure reached 27 inches Hg is plotted as a function of Na molarity in Figure 10 through Figure 12. The curves for Envelopes A and B are similar. The curve for Envelope C differs from the other two in that it exhibits a lower volatility for all except the higher Na M mixtures. Such a trend demonstrates that something other than sodium is responsible for decreasing the volatility of the mixtures, at least at lower Na M concentrations. Envelope C contains significant amounts of organics and complexants while Envelopes A and B contain only small amounts of organics and no complexants.

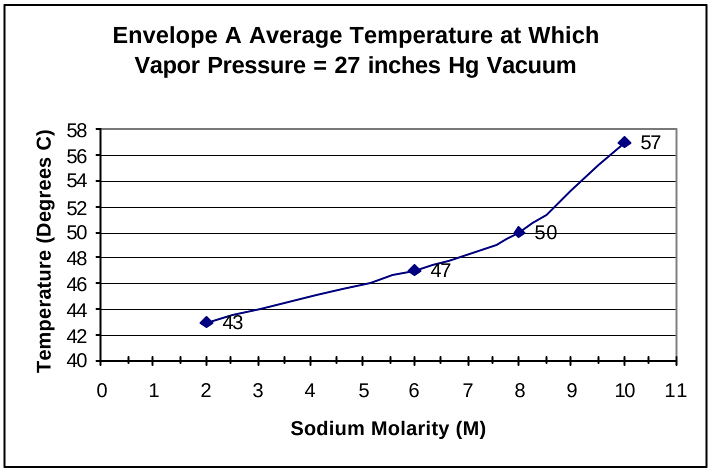

Figure 10. Envelope A Temperature Vs. Na M @ 27 inHg

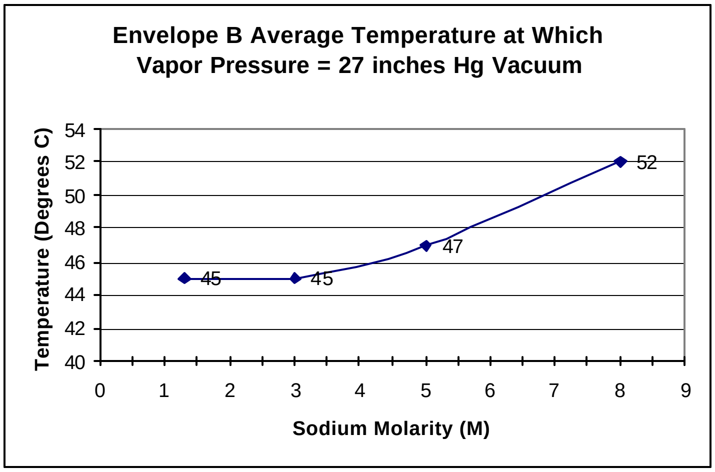

Figure 11. Envelope B Temperature Vs. Na M @ 27 inHg

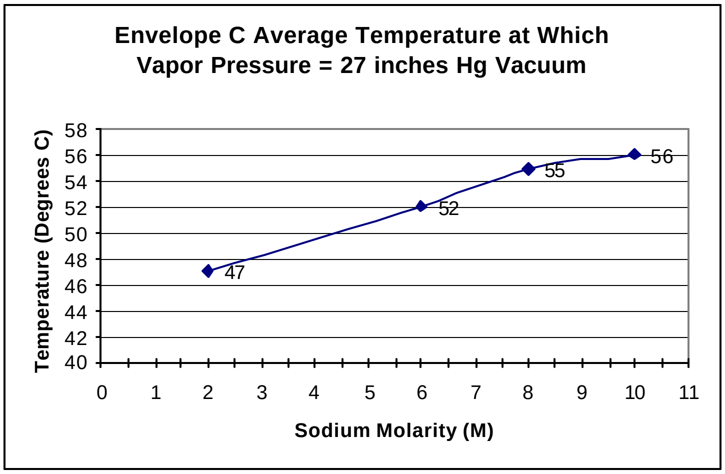

Figure 12. Envelope C Temperature Vs. Na M @ 27 inHg

3.5.3 Viscosity

In Appendix A, Figure A-17 through Figure A-28 illustrate viscosities of Envelope A, B, and C mixtures at 15, 25, and 60°C. As a function of temperature, viscosities of all three waste envelopes increase parabolically as temperature increases. For all three envelopes, mixture ratios had little impact on viscosity. However, temperature and sodium molarity had a noticeable affect on viscosity. It is observed that there is a progressively larger spread in viscosities at higher temperatures as Na molarity increases. For example, for 2 molar Na mixtures, viscosities are virtually superimposed throughout the entire range of 15°C to 60°C. However, for 6 molar mixtures, as temperature increases, viscosities begin to spread apart with the largest spread at 60°C. Consequently, an even larger variance is observed in 8 molar mixtures at the higher range of 60°C. Empirically derived formulas and fitting parameters for viscosities of Envelope A, B, and C are listed in Table 13.

Table 13. Empirically Derived Formulas of Viscosities

Waste Envelope Mixtures	Formula	Fitting Parameter **a**	Fitting Parameter **b**	R^2
Envelope A	$y = \exp(a + bx^{1.5})$	0.12505507	0.063814051	0.95625583
Envelope B	$y = \exp(a + bx^{1.5})$	0.11400429	0.066030271	0.94493978
Envelope C	$y = \exp(a + bx^{1.5})$	0.050724972	0.10209671	0.98134846

3.5.4 Heat Capacity and Thermal Conductivity

Heat capacities and thermal conductivities of Envelope A, B, and C mixtures are presented in Figure A-37 through Figure A-39. There existed a large decrease in the heat capacities of Envelope A mixtures between 2 and 6 M Na samples, but an almost nonexistent decrease between 6 and 8 M Na mixtures. On average, all heat capacities for all three waste envelopes were lower than the heat capacity of water at 20°C (0.968 cal/g·K—measured). On an average, Envelope C heat capacities were higher than Envelope B heat capacities. For each envelope, a slow decline in heat capacities was observed as Na M increased. On an average, thermal conductivities of all three waste envelopes congregated around the thermal conductivity of water (0.598 W/m·C—measured) ± 0.2 W/m·C.

3.5.5 Solubility, Solids Analysis, and NAS Formation

The physical properties of mixtures and individual recycle streams of Envelope A, B, and C LAW waste simulants with SBS recycles were measured over time to characterize their solubilities and to determine if sodium aluminosilicates formed. Since each mixture already contained solids, solubility ranges were determined by measuring volume percent centrifuged and weight percent solids of mixtures at different measured sodium molarities and temperatures (see Table 14 for a solubility summary). The method to determine solubility will be discussed in relation to Figure 13 for Envelope A SM-55-11 simulant. To determine the solubility range for Envelope A mixture SM-55-11, the Na molarity in volume percent graphs is examined visually to determine when significant precipitation begins. Labels A (7 M Na)[29] and C (7 M Na) in Figure 13 are points at which precipitation (significant increase in solids) begins for volume and weight percent solids, respectively. Labels B (7.5 M Na) and D (7.5 M Na) in Figure 13 are points at which precipitation begins to end for volume and weight percent solids, respectively. Weight percent graphs were used to verify solubility ranges determined by volume percent graphs for SM-55-11. Hence, the solubility range for SM-55-11 at 25°C is approximately 7 M Na to 8 M Na. SRTC was unable to accurately determine solubility ranges at 15 and 50°C since no available instrumentation allowed sample temperatures to be consistently maintained throughout such measurements. Figure A-40 through Figure A-73 in Appendix A give visual representations of Na molarity ranges in which significant amounts of precipitation occurred. The percent precipitated solids was determined by first calculating the theoretical amount of solids that should have formed and then subtracting that quotient from the actual amount of solids formed.

Table 14. Solubility Ranges for Envelopes A, B, and C

Waste Envelope	Simulant Mixtures	Solubility Range Approximation (Na M)
A	SM-55-01	7-8
	SM-55-02	7.5-8
	SM-55-03	6-6.5
	SM-55-04	6.5-7.5
	SM-55-05	7.5-8
	SM-55-06	8.5-9
	SM-55-07[30]	Not Measured
	SM-55-08	6.5-7
	SM-55-09	8+
	SM-55-10	8-8.5
	SM-55-11	7-7.5
	SM-55-12	7-7.5
	AP101	7-7.5
B	AZ101-70	~7
	AZ102-70	7-7.5
	AZ101-60	6.5-7
	AZ102-60	5-5.5
C	AN102-55	7.5-8
	AN107-55	8-8.5
	AN102-43	8-8.5
	AN107-43	8-8.5

---

[29] Approximations

[30] SM-55-07 mixtures formed gels. Thus, experimentation with these mixtures was discontinued.

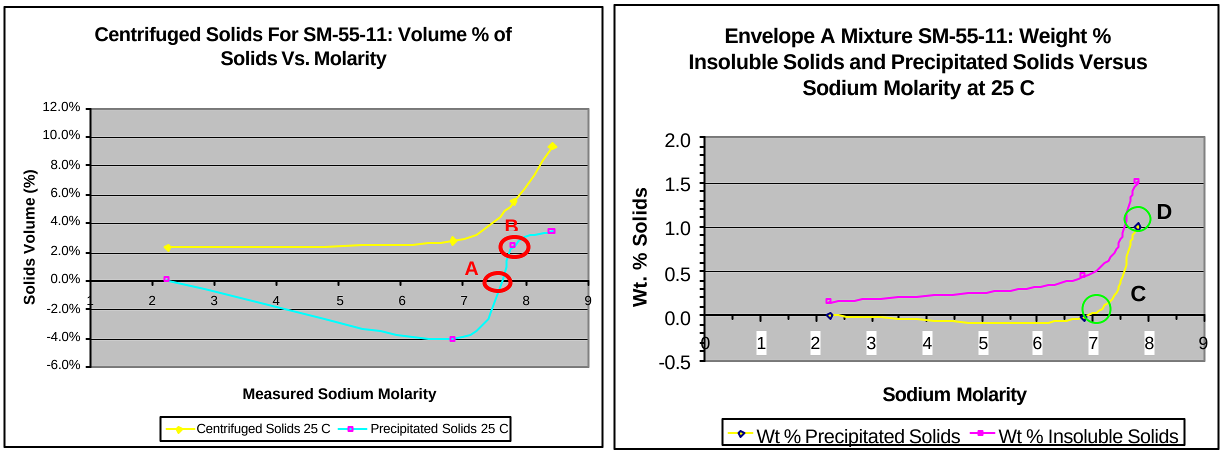

Figure 13. Solubility Range: Method of Determination

That difference was divided by the total volume of that mixture, giving volume percent precipitated solids. Trends of precipitated solids that have a slope near zero indicate no precipitation occurred while negative Y-values or slopes suggest instances in which some insoluble solids were dissolved. Other reasons for negative slopes or points may be due to denser packing of solids whose crystal morphologies had changed.

The presence of sodium aluminosilicates was studied at 50°C to determine their formation relative to the quantity of time each mixture existed. The waste and recycle streams were mixed and the resulting 16 mixtures were held in 50°C shaker baths for 4, 8, 16, and 24 hr periods (see Table 15). No NAS was found prior to 24 hours in the samples tested. NAS was found in Envelope A simulant SM-55-03 at 24 hours after mixing and in many other mixtures held for periods greater than 24 hours. In separate testing, 6, 7, 8, and 8.5 M Na[31] Envelope C mixtures with 43% SBS were held in a Precision® reciprocal shaker bath at 50°C for 7 days. XRD results revealed that cancrinite ($Na_6CaAl_6Si_6(CO_3)O_{24}\cdot 2H_2O$), a sodium aluminosilicate, had formed in the 6 and 7 molar samples (see Table 16); however, no NAS was detected in the 8 and 8.5 molar samples. In respect to such information, NAS is not likely to form as crystals in the treated feed evaporator, but more likely to form later in the melter feed system. Furthermore, although the presence of NAS solids was not found in mixtures prior to 24 hours, it is possible that NAS existed as a homogeneous gel. Table 17, Table 18, and Table 19, show Envelope A, B, and C (respectively) solids from mixtures older than 7 days that were identified by XRD analysis (see Figure A-78 for chemical names of solids). The presence of various forms of NAS was found throughout Envelope A and C blends and even waste feed simulants (≥ 7 days). No NAS were found in Envelope B mixtures or waste feed simulants sent in for XRD analysis. Figure A-79 through Figure A-82 show distributions of solids found by XRD analysis of Envelope A, B, and C mixtures. Figure A-83 through Figure A-85 display frequencies of solids that appeared in A, B, and C mixtures.

---

[31] Target molarity values

Table 15. NAS Formation Per Time at 50 C

Time Held at 50°C (hr)	Envelope A, B, C Mixtures	NAS Present? If Yes, Which?
4	SM-55-01, SM-55-03, AZ101-70, AN102-55	No
8	SM-55-01, SM-55-03, AZ101-70, AN102-55	No
16	SM-55-01, SM-55-03, AZ101-70, AN102-55	No
24	SM-55-01, **SM-55-03**, AZ101-70, AN102-55	Yes, **SM-55-03**

Table 16. 43% SBS Envelope C Samples Held at 50°C for 7 Days

Sample (Waste-%SBS-TargetNaM-Temperature)	Solids Found by XRD
AN107-43-6M-50	NaNO3, Na3H(CO3)2!2H2O, SiO2, **Na6CaAlSi6(CO3)O24!2H2O**
AN107-43-7M-50	NaNO3, Na3H(CO3)2!2H2O, SiO2, **Na6CaAlSi6(CO3)O24!2H2O**, SiO2, Na6CaAlSi6(CO3)O24!2H2O, Na3FSO4
AN107-43-8M-50	NaNO3, Na3H(CO3)2!2H2O, SiO2, Na3FSO4, Na2CO3!H2O
AN107-43-8.5M-50	NaNO3, Na3H(CO3)2!2H2O, Na3FSO4, Na2CO3!H2O

Table 17. XRD Analysis of Solids in Envelope A Mixtures Held Over 7 Days[32]

Simulants and Mixtures	Waste Composition (XRD)	2 M Na (Initial Mix)	8 M Na	8.5 M Na	9.5 M Na
SM-01	Na2Ca(CO3)2!2H2O, B-Al(OH)3, G-Al(OH)3, Na2CO3!H2O, NaNO3,	N/A	N/A	N/A	N/A
SM-55-01		SiO2, Na2CO3!H2O, **NaAlSiO4**, B-Al(OH)3,	(Al2Li(OH)6)2CO3!xH2O, NaNO3, NaNO2, Na7F(PO4)2(H2O)19,	N/A	N/A
SM-02	NaF, **Na96Al96Si96O384!216H2O**, C2Na2O4	N/A	N/A	N/A	N/A
SM-55-02		SiO2,	N/A	N/A	(Al2Li(OH)6)2CO3!xH2O, NaNO3, SiO2, Na2CO3!H2O, NaNO2, Na7F(PO4)2(H2O)19, Na3FSO4,
SM-03	**Na96Al96Si96O384!216H2O**, NaNO3	N/A	N/A	N/A	N/A
SM-55-03		(Al2Li(OH)6)2CO3!xH2O, SiO2, **NaAlSiPO4!xH2O**,	N/A	(Al2Li(OH)6)2CO3!xH2O, NaNO3, SiO2, Na2CO3!H2O, NaNO2, Na7F(PO4)2(H2O)19,	N/A
SM-04	Na7F(PO4)2(H2O)19, NaF, C2Na2O4	N/A	N/A	N/A	N/A
SM-55-04		SiO2, Na2CO3!H2O,	N/A	(Al2Li(OH)6)2CO3!xH2O, NaNO3, LiAlF(PO4), SiO2, Na2CO3!H2O, Na7F(PO4)2(H2O)19, Na3FSO4, NaF, **Na8[AlSiO4]6(NO3)2**,	N/A

---

[32] B-Al(OH)3 = Bayerite; G-Al(OH)3 = Gibsite

Table 17 (continued). XRD Analysis of Solids in Envelope A Mixtures Held Over 7 Days

Simulants and Mixtures	Waste Composition (XRD)	2 M Na (Initial Mix)	8 M Na	8.5 M Na	9 M Na
SM-05	NaNO3, Na2Ca(CO3)2!2H2O, Na3H(CO3)2(H2O)2, Na6(CO3)2SO4	N/A	N/A	N/A	N/A
SM-55-05		SiO2, Na2CO3!H2O,	N/A	(Al2Li(OH)6)2CO3!xH2O, NaNO3, AlF3H2O, LiAlF(PO4), SiO2, Na2CO3!H2O, **Na5Al3CSi3O15**,	N/A
SM-06	NaNO3, **Na2Al2Si1.85O7.7!5.1H2O**, Na3H(CO3)2!2H2O, B-Al(OH)3	N/A	N/A	N/A	N/A
SM-55-06		(Al2Li(OH)6)2CO3!xH2O, NaNO3, SiO2, **NaAlSiPO4!xH2O**,	N/A	N/A	(Al2Li(OH)6)2CO3!xH2O, NaNO3, SiO2, Na2CO3!H2O, NaNO2, Na7F(PO4)2(H2O)19,
SM-07	(Na3.25(OH).25(H2O)12)(PO4), Na2CO3!H2O	N/A	N/A	N/A	N/A
SM-55-07		(Al2Li(OH)6)2CO3!xH2O, SiO2, Na2CO3!H2O, B-Al(OH)3, Na3FSO4,	(Al2Li(OH)6)2CO3!xH2O, NaNO3, SiO2, Na2CO3!H2O, Na7F(PO4)2(H2O)19,	N/A	N/A
SM-08	C2Na2O4, **Na96Al96Si96O384!216H2O**, NaNO3	N/A	N/A	N/A	N/A
SM-55-08		(Al2Li(OH)6)2CO3!xH2O, NaNO3, SiO2, **NaAlSiPO4!xH2O**,	N/A	NaNO3, SiO2, NaNO2, Na7F(PO4)2(H2O)19, Na3FSO4, **Na8[AlSiO4]6(NO3)2**, Na2C2O4,	N/A

Table 17 (continued). XRD Analysis of Solids in Envelope A Mixtures Held Over 7 Days

Simulants and Mixtures	Waste Composition (XRD)	2 M Na (Initial Mix)	8 M Na
SM-09	NaF, **Na96Al96Si96O384 !216H2O**, NaNO3, Na2CO3!H2O	N/A	N/A
SM-55-09		(Al2Li(OH)6)2CO3!xH2O, NaNO3, SiO2, B-Al(OH)3,	(Al2Li(OH)6)2CO3!xH2O, NaNO3, Na3FSO4,
SM-10	NaF, **Na96Al96Si96O384 !216H2O**, NaNO3, Na2CO3!H2O, B-Al(OH)3, G-Al(OH)3	N/A	N/A
SM-55-10		(Al2Li(OH)6)2CO3!xH2O, SiO2, Na2CO3!H2O, B-Al(OH)3,	(Al2Li(OH)6)2CO3!xH2O, NaNO3, SiO2, Na2CO3!H2O, NaNO2, Na7F(PO4)2(H2O)19, Na3FSO4, NaF,
SM-11	Na7F(PO4)2(H2O)19, NaF, C2Na2O4	N/A	N/A
SM-55-11		N/A	(Al2Li(OH)6)2CO3!xH2O, NaNO3, SiO2, Na2CO3!H2O, Na3FSO4, NaF, **Na5Al3CSi3O15**,
SM-12	Na7F(PO4)2(H2O)19, NaF, C2Na2O4	N/A	N/A
SM-55-12		(Al2Li(OH)6)2CO3!xH2O, SiO2, Na2CO3!H2O, **NaAlSiO4**, B-Al(OH)3, NaNO2,	Na7F(PO4)2(H2O)19, Na3FSO4,

Table 18. XRD Analysis of Solids in Envelope B Mixtures Held Over 7 Days

Simulants and Mixtures	Waste Composition (XRD)	1.2 M Na	1.3 M Na	5.5 M Na
AZ101 Sup	NH4NO3, CsNO3, ZrO(NO3)2!xH20, KNO3, NaCl, NaF, Na2CrO4, Na2SO4, Al(OH)3, NaOH, Na3PO4!12H20, Na2CO3, NaNO3, NaNO2,	N/A	N/A	N/A
AZ101-70	N/A	(Al2Li(OH)6)2CO3!xH2O, SiO2, B-Al(OH)3,	N/A	(Al2Li(OH)6)2CO3!xH2O, NaNO3, SiO2, B-Al(OH)3, G-Al(OH)3, Na3FSO4
AZ102 Sup	N/A	N/A	N/A	N/A
AZ102-70	N/A	(Al2Li(OH)6)2CO3!xH2O, SiO2, KCl,	N/A	(Al2Li(OH)6)2CO3!xH2O, SiO2, NaNO2, Na3FSO4, Na3AlF6
AZ101 Sup	NH4NO3, CsNO3, ZrO(NO3)2!xH20, KNO3, NaCl, NaF, Na2CrO4, Na2SO4, Al(OH)3, NaOH, Na3PO4!12H20, Na2CO3, NaNO3, NaNO2,	N/A	N/A	N/A
AZ101-60	N/A	N/A	(Al2Li(OH)6)2CO3!xH2O, SiO2, KCl,	(Al2Li(OH)6)2CO3!xH2O, NaNO3, B-Al(OH)3, Na3FSO4
AZ102 Sup	N/A	N/A	N/A	N/A
AZ102-60	N/A	N/A	N/A	(Al2Li(OH)6)2CO3!xH2O, Na3FSO4,

Table 19. XRD Analysis of Solids in Envelope C Mixtures Held Over 7 Days

Simulants and Mixtures	2 M Na	6.5 M Na	8 M Na	8.5 M Na
pAN102	N/A	N/A	N/A	N/A
AN102-55	(Al2Li(OH)6)2CO3!xH2O, NaNO3, SiO2, KCl,	N/A	(Al2Li(OH)6)2CO3!xH2O, NaNO3, SiO2, Na2CO3!H2O, NaNO2, Na7F(PO4)2(H2O)19, Na3FSO4,	N/A
pAN107	N/A	N/A	N/A	N/A
AN107-55	(Al2Li(OH)6)2CO3!xH2O, NaNO3, SiO2, KCl,	N/A	N/A	NaNO3, SiO2, Na2CO3!H2O, Na3FSO4, **Na5Al3CSi3O15**, Na2Ca(CO3)2!2H2O
pAN102	N/A	N/A	N/A	N/A
AN102-43	(Al2Li(OH)6)2CO3!xH2O, NaNO3, SiO2, **NaAlSiPO4!xH2O**, NaNO2, Na3FSO4	(Al2Li(OH)6)2CO3!xH2O, NaNO3, SiO2, Na2CO3!H2O, **Na5Al3CSi3O15**	(Al2Li(OH)6)2CO3!xH2O, NaNO3, SiO2, Na2CO3!H2O, Na7F(PO4)2(H2O)19, Na3FSO4	N/A
pAN107	N/A	N/A	N/A	N/A
AN107-43	NaNO3, SiO2,	N/A	SiO2,	NaNO3, SiO2, Na2CO3!H2O, Na3FSO4, **Na5Al3CSi3O15**, Na2Ca(CO3)2!2H2O

3.6 COMPARISON OF TREATED FEED SOLUBILITY STUDIES WITH PREVIOUS STUDIES

Previous work from several reports pertaining to solubilities of Envelope A, B, and C simulants has been reviewed. No previous solubility studies were found concerning AZ102 simulant. Table 20 displays Na concentrations of simulants (previous studies) and blends (current studies) at which significant amounts of solids precipitated. For the comparison, since simulant and recycle blends had not been previously investigated to such an extent, the blends with the lower percentages of SBS (higher % waste simulant) were used. Similar solids such as Na_3FSO_4 $Na_2CO_3 \cdot H_20$, and $Na_7F(PO_4)_2 \cdot 19H_20$ were found in current solubility studies as in previous studies of simulants at comparable Na concentrations.

Table 20. Solubility Ranges and Major Precipitated Solids of Treated Feed Studies and Previous Studies

Waste Simulants	Previous Study Solubility Point	Major Precipitated Solids	Waste Simulants + SBS Recycle	Current Study Solubility Range	Major Precipitated Solids
	Na M (25°C)			Na M (25°C)	
AZ101[33]	7.3	Na_3FSO_4	AZ101-60% SBS	6.5 - 7	$NaNO_3$, Na_3FSO_4
AN102[34]	8.2	$Na_2CO_3 \cdot H_2O$, $Na_2C_2O_4$, $Na_3H(CO_3)(H_2O)_2$, $Na_7F(PO_4)_2 \cdot 19H_2O$	AN102-43% SBS	8 - 8.5	$Na_2CO_3 \cdot H_20$, $Na_7F(PO_4)_2 \cdot 19H_20$
AN107[35]	10.1 (50°C)	$Na_2CO_3 \cdot 10H_2O$, $NaNO_3$	AN107-43% SBS	8 - 8.5	$Na_2CO_3 \cdot H_20$, Na_3FSO_4

3.7 FOAMING

The foaming tendencies of Envelope A, B, and C mixtures were noted during evaporations. At an average evaporation rate of approximately 5.5 ml/min, no significant amount of foaming was observed during normal boiling (see Figure 14).[18] After boiling for sustained periods of time (1-3 hrs), samples for physical properties were pulled from the evaporator. Upon returning to operating vacuum (27” Hg), the mixture remaining in the evaporator vessel would initially foam to approximately 500% of the liquid level. After 30 to 60 seconds, foam would readily subside to less than 50% and normal boiling would resume. It was observed that bubbles at initial foaming were very small in diameter (about a quarter inch) while the bubbles at the end of initial foaming were two to three times as large in diameter. Since such foaming only occurred for a few seconds and only upon returning to evaporating conditions, it is concluded that the cause of such foaming is due simply to the inadvertent superheating of the warm mixture by the sudden decrease of pressure within the vessel as vacuum is initially applied. Therefore in the plant process, it is recommended that whenever vacuum is released, steam is also temporarily discontinued to prevent superheating conditions.

---

[33] Calloway, T. B. Jr., Choi, A. S., Monson, P. R., Evaporation of Hanford Envelope B Simulant (AZ101) Preliminary Report, BNF-003-98-0166, Rev. 1, Savannah River Site, Aiken, SC 29808 (2000).

[34] Crowder, M. L., Crawford, C. L., et. al., Bench-Scale Evaporation of a Large Hanford Envelope C Sample (Tank 241-AN-102), WSRC-TR-2000-00469, SRT-RPP-2000-00043 Rev. 1, Savannah River Site, Aiken, SC 29808 (2001).

[35] Saito, H. H., Calloway T. B. Jr., et. al., AN-107 (C) Simulant Bench-Scale LAW Evaporation with Organic Regulatory Analysis , WSRC-TR-2000-00486, SRT-RPP-2000-00047, BNF-003-98-0275, Savannah River Site, Aiken, SC 29808 (2001).

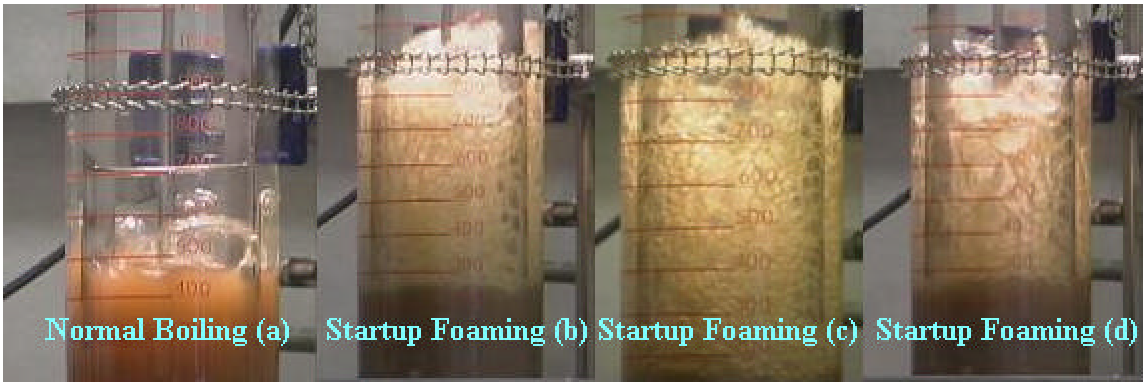

Figure 14. Typical Startup Foaming for Envelope A, B, and C Mixtures

4.0 FUTURE WORK

Future work is recommended in the following areas:

- Solids (e.g. Lithium aluminum carbonate hydroxide hydrate) formed in the LAW solutions that are not currently in the OLI Public database should be added and modeling studies conducted to determine the total quantity of these solids expected to precipitate in the Treated Feed Evaporator system.

- If scaling or buildup of solids occurs in the WTP pilot evaporator, bench scale cleaning and scaling studies should be conducted to determine the most appropriate cleaning method, disposal route, and downstream effects of the chosen cleaning solution.

5.0 APPENDIX A

As frequently alluded to within the body of this report, this section contains data regression for densities, vapor pressures, viscosities, heat capacities, thermal conductivities, solubility curves for volume % and precipitated solids, curves for weight percent solids, rheology calibrations with water, distributions of solids, and frequency of solids for Envelope A, B, and C waste simulants and blends.

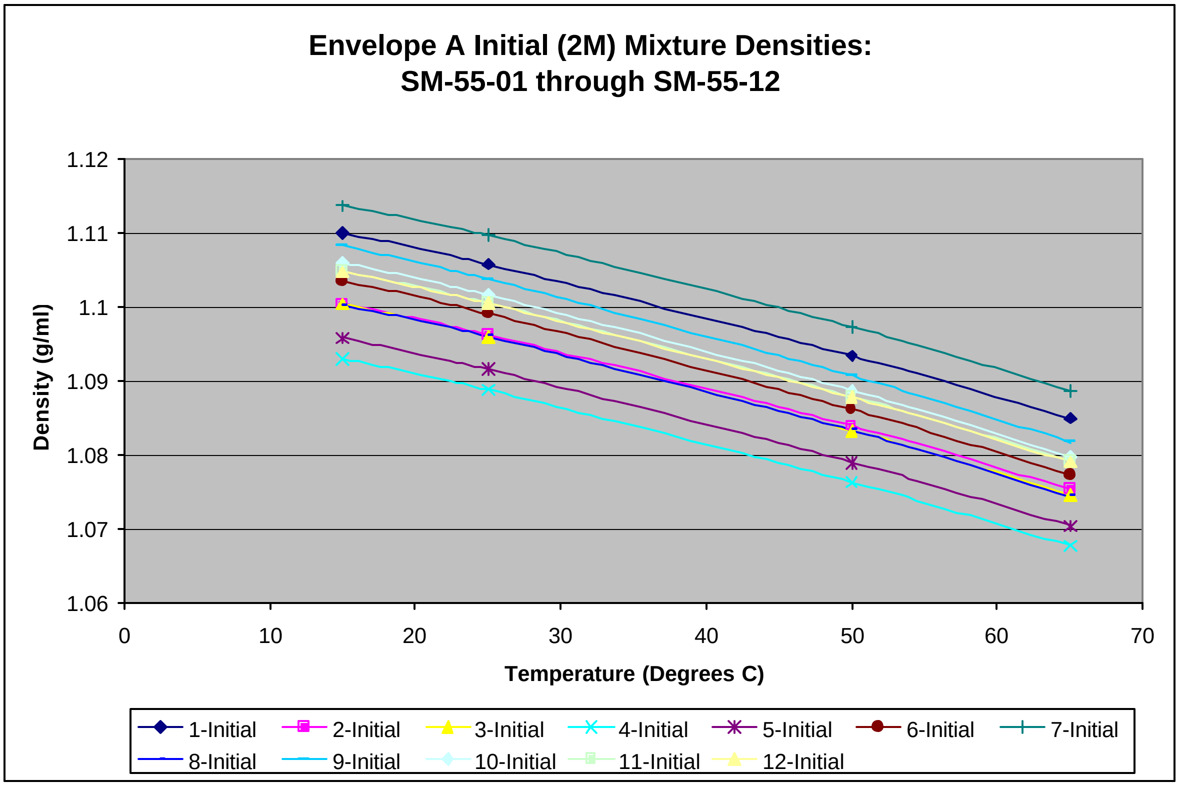

Figure A-1. Densities of Envelope A Initial (2M) Mixtures

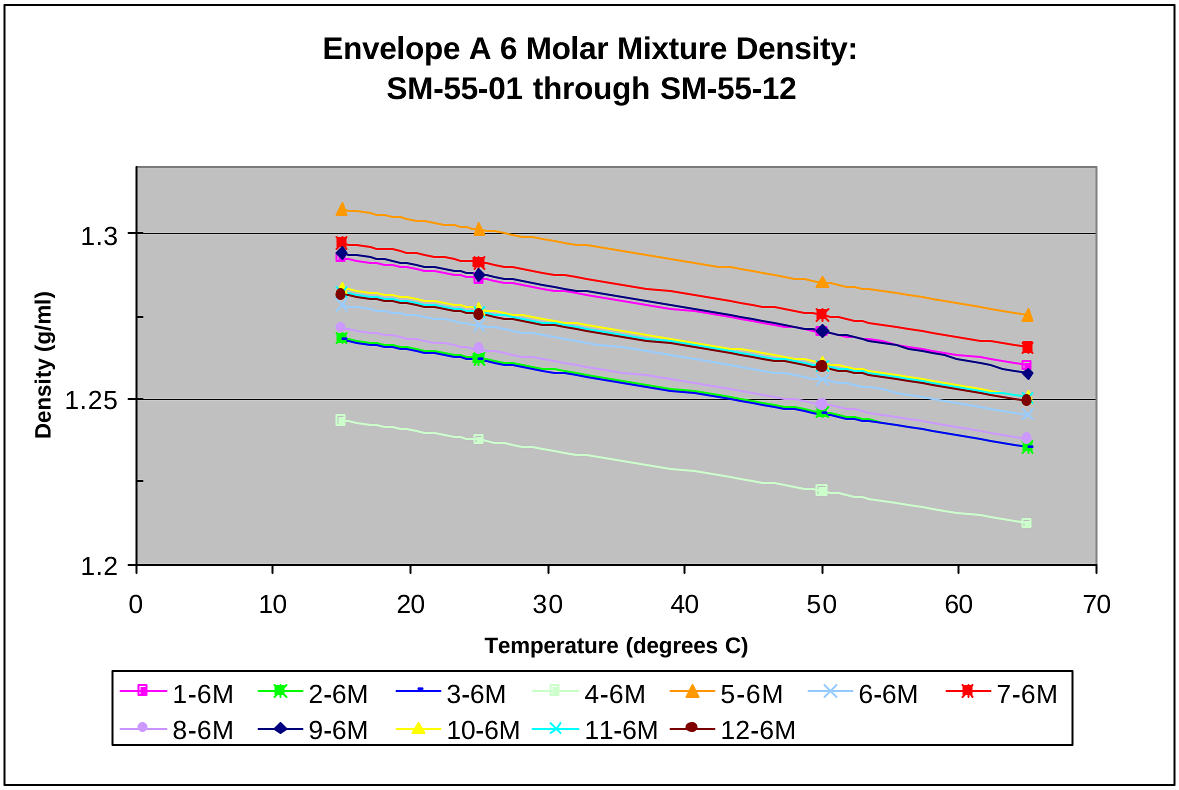

Figure A-2. Densities of Envelope A 6M Mixtures

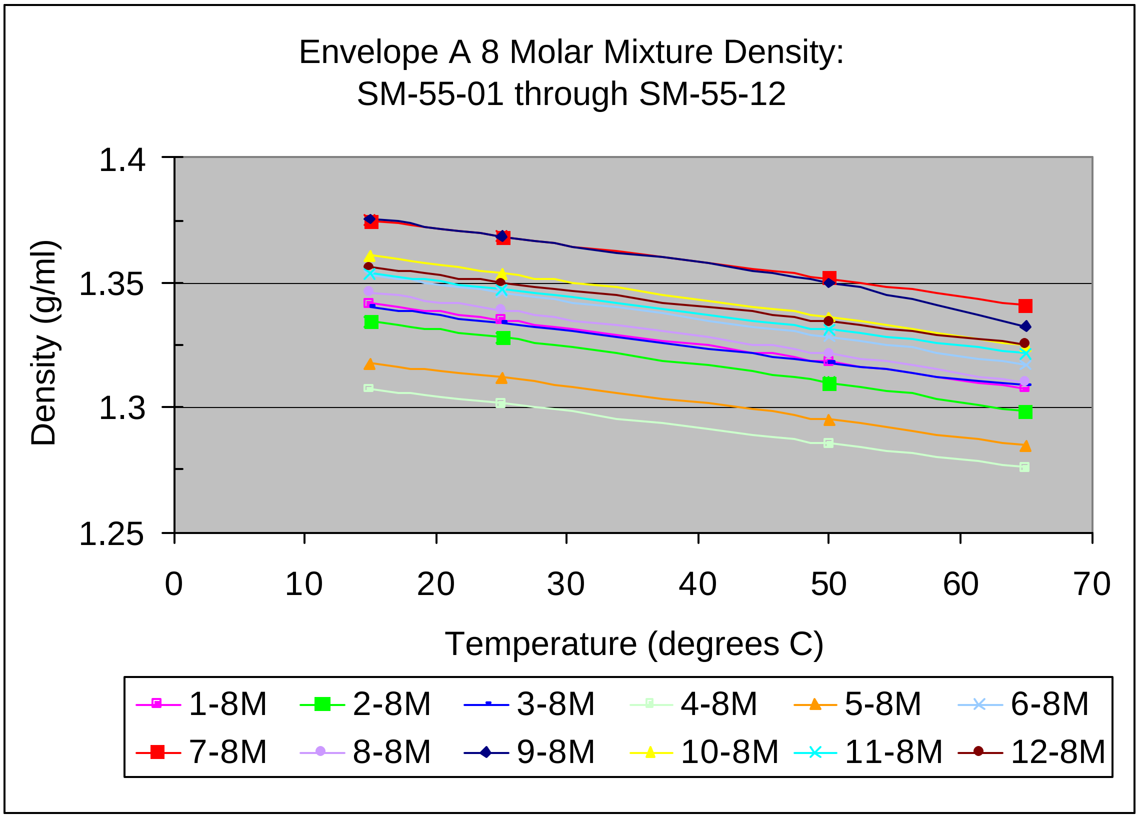

Figure A-3. Densities of Envelope A 8M Mixtures

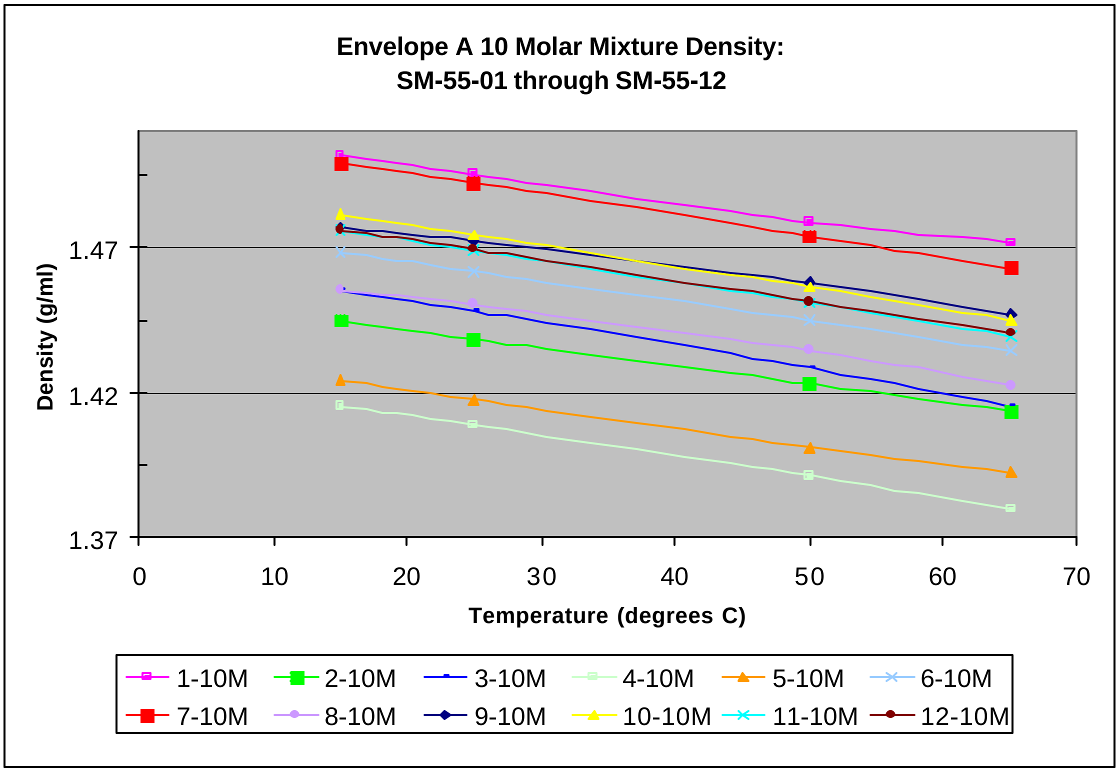

Figure A-4. Densities of Envelope A 10M Mixtures

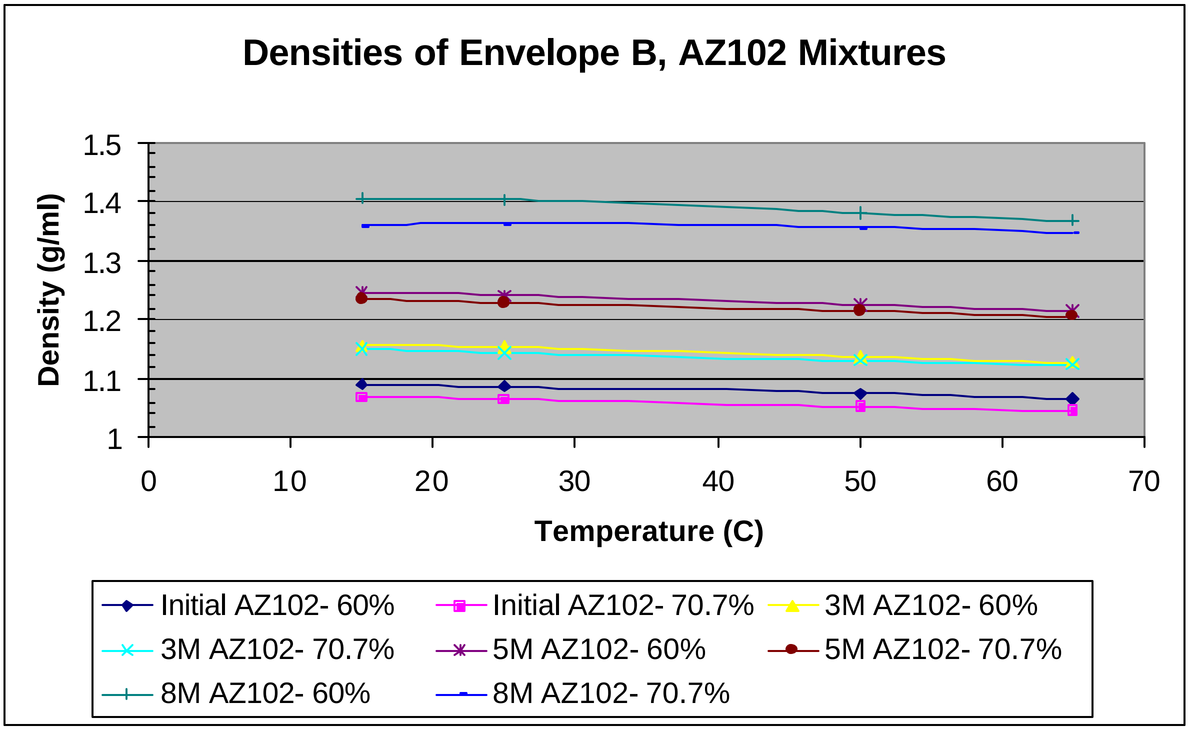

Figure A-5. Densities of Envelope B, AZ101 Mixtures

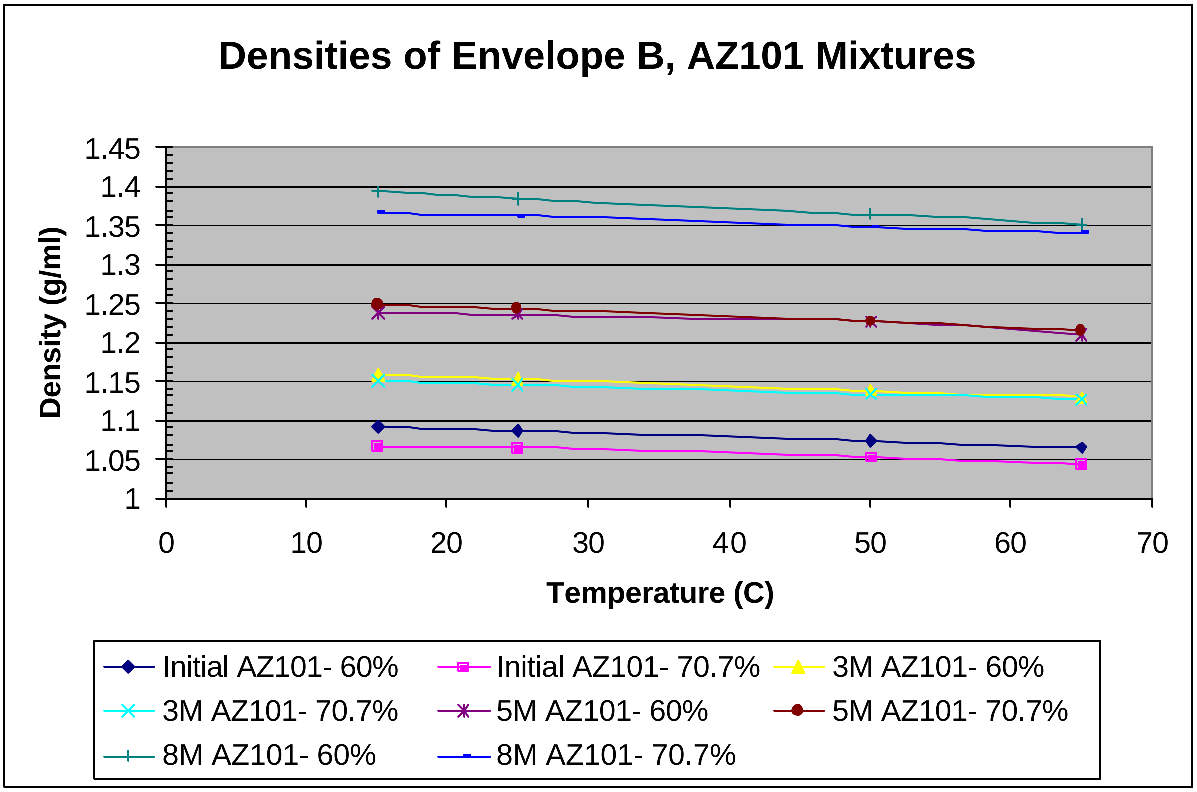

Figure A-6. Densities of Envelope B, AZ102 Mixtures

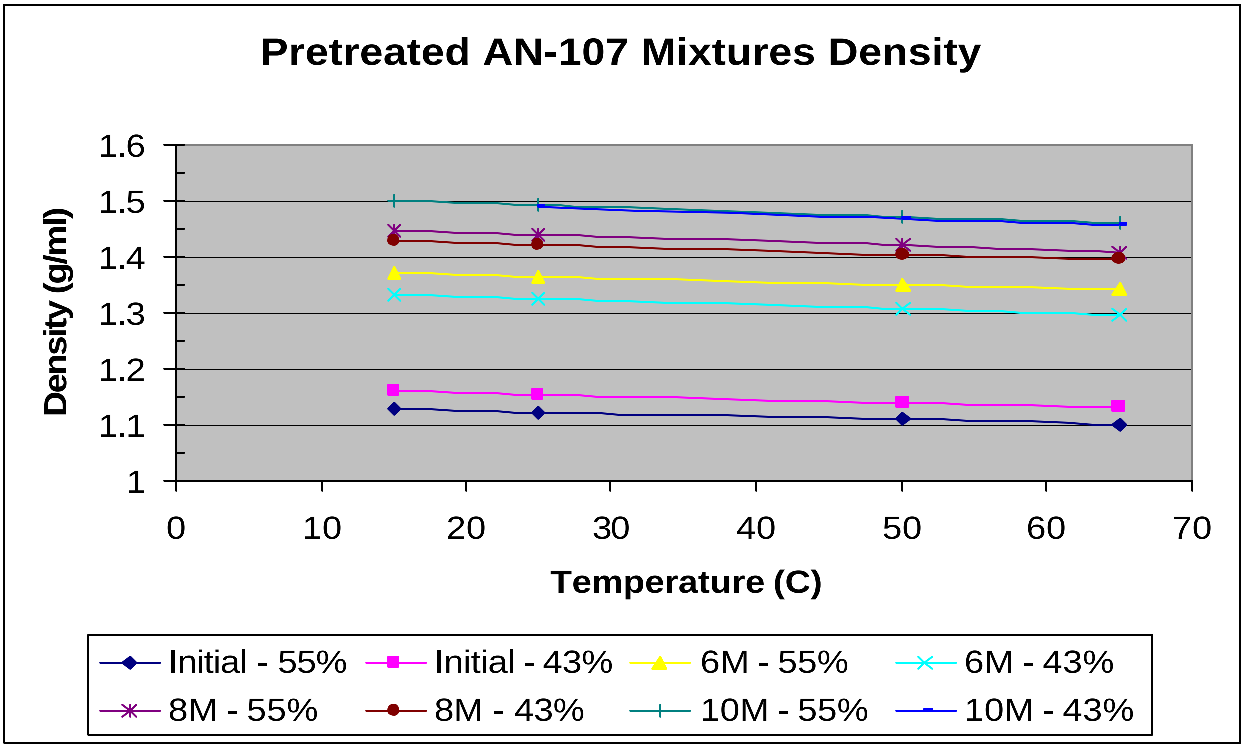

Figure A-7. Densities of Envelope C, Pretreated AN107 Mixtures

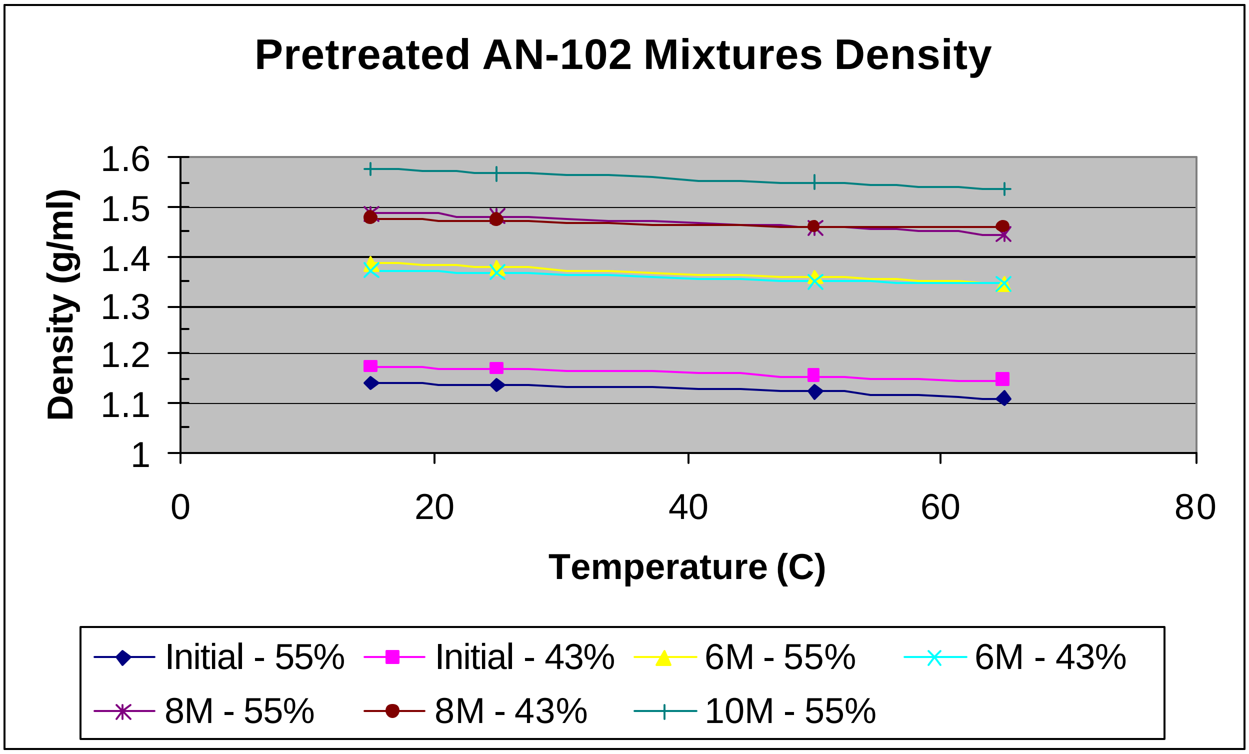

Figure A-8. Densities of Envelope C, Prtreated AN102 Mixtures

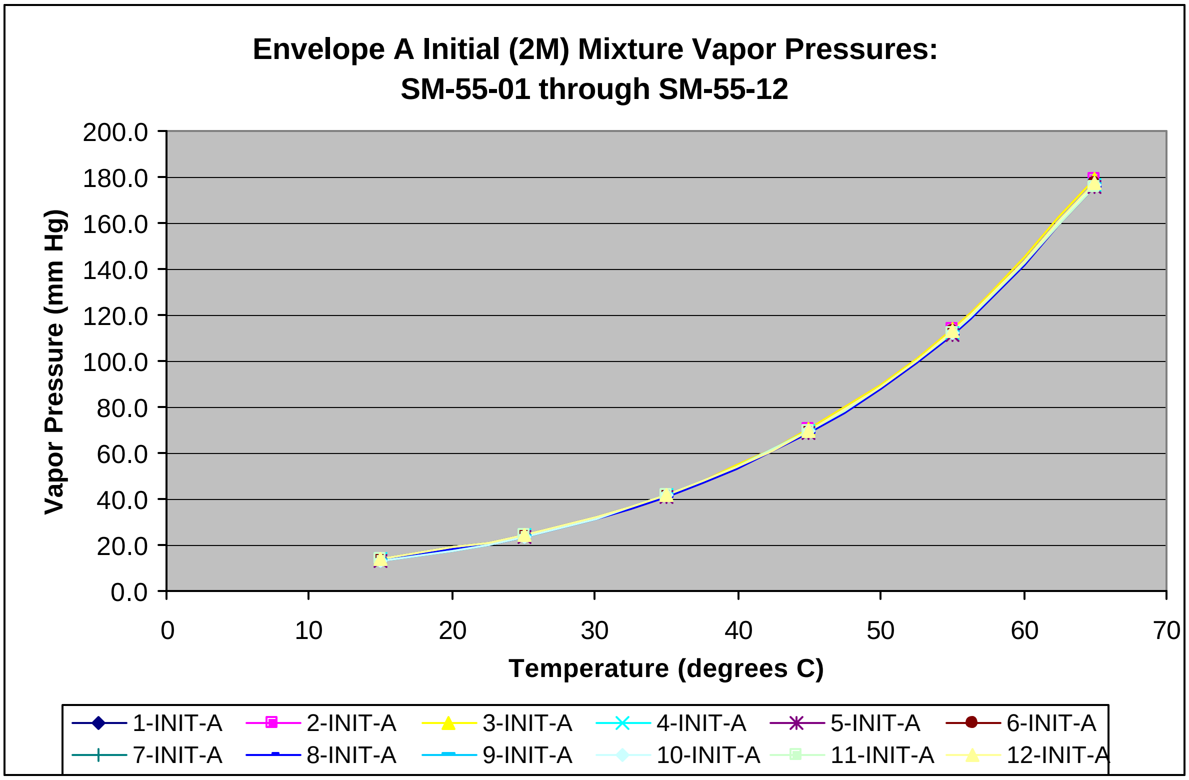

Figure A-9. Vapor Pressures of Envelope A Initial (2M) Mixtures

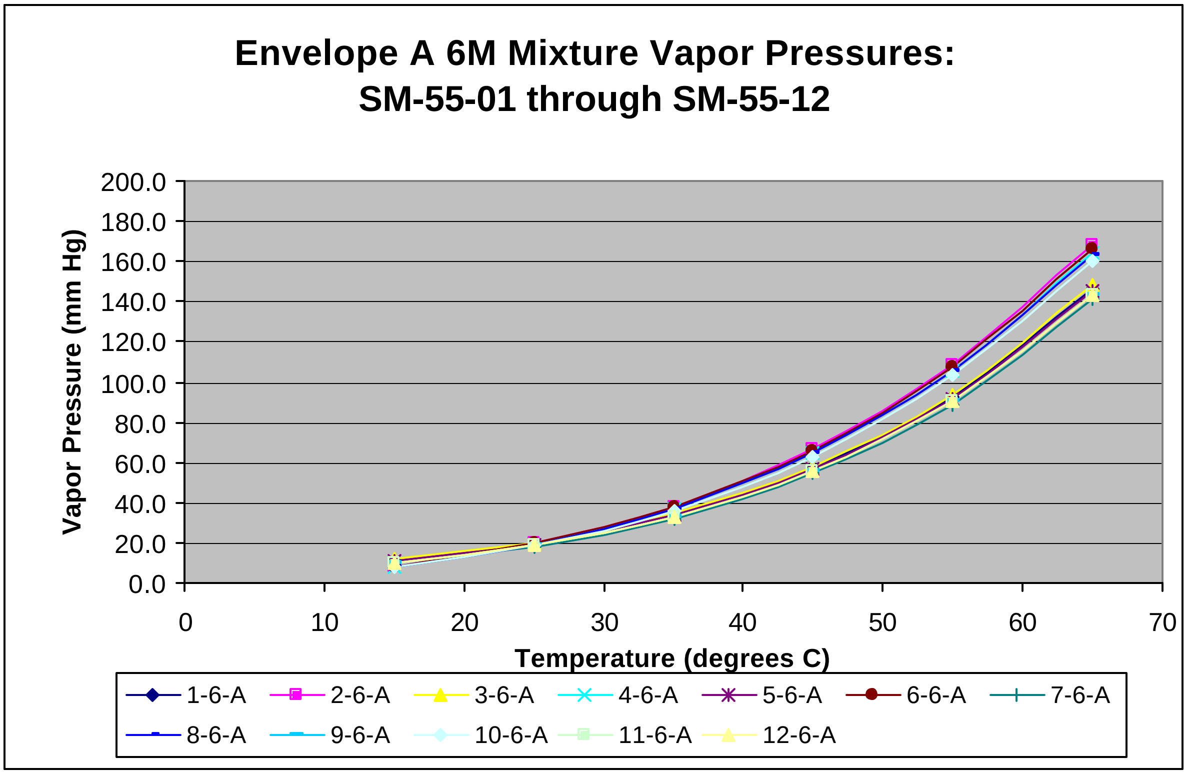

Figure A-10. Vapor Pressures of Envelope A 6M Mixtures

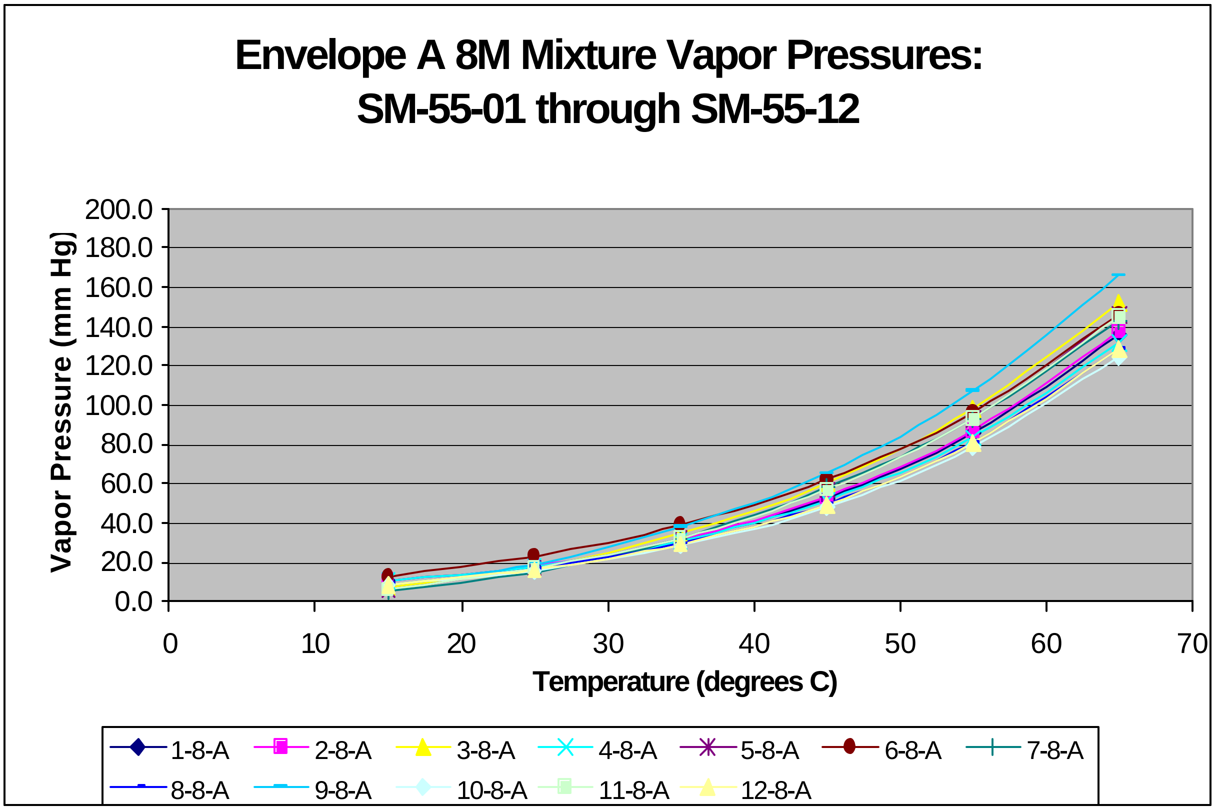

Figure A-11. Vapor Pressures of Envelope A 8 M Mixtures

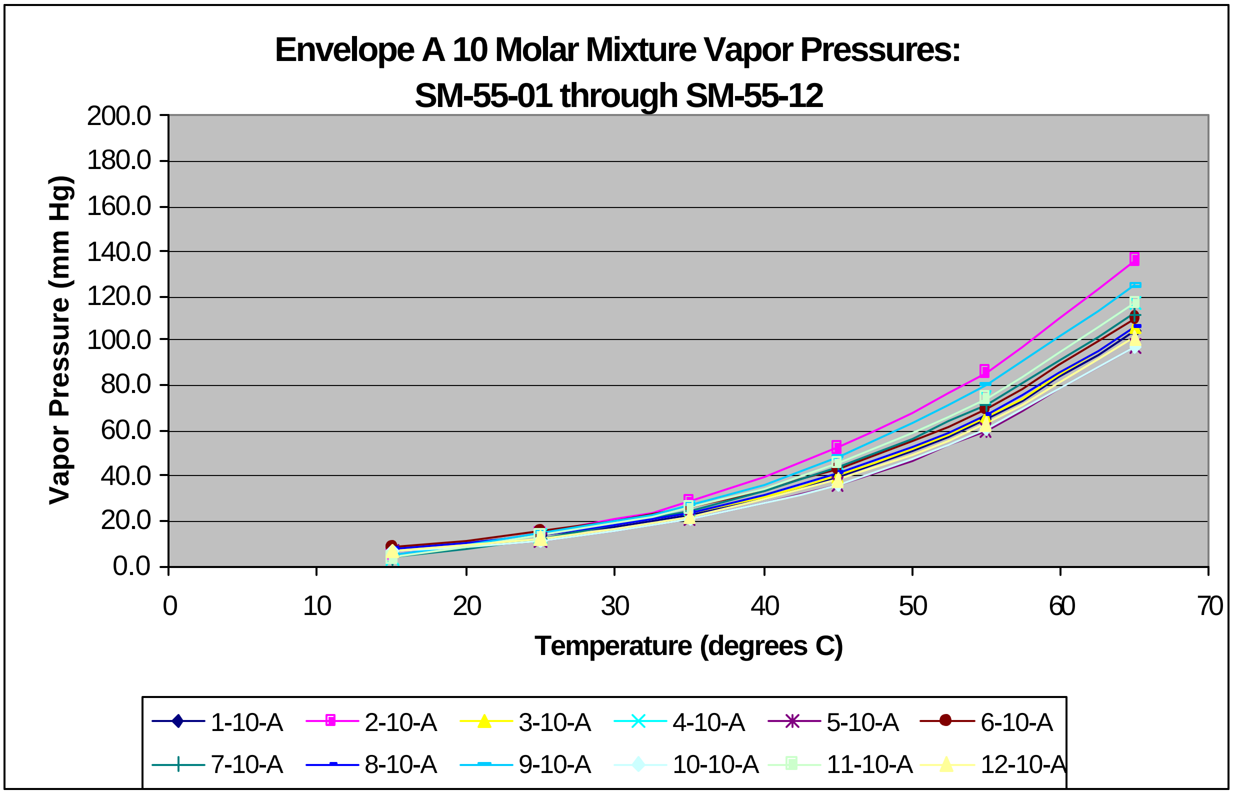

Figure A-12. Vapor Pressures of Envelope A 10 M Mixtures

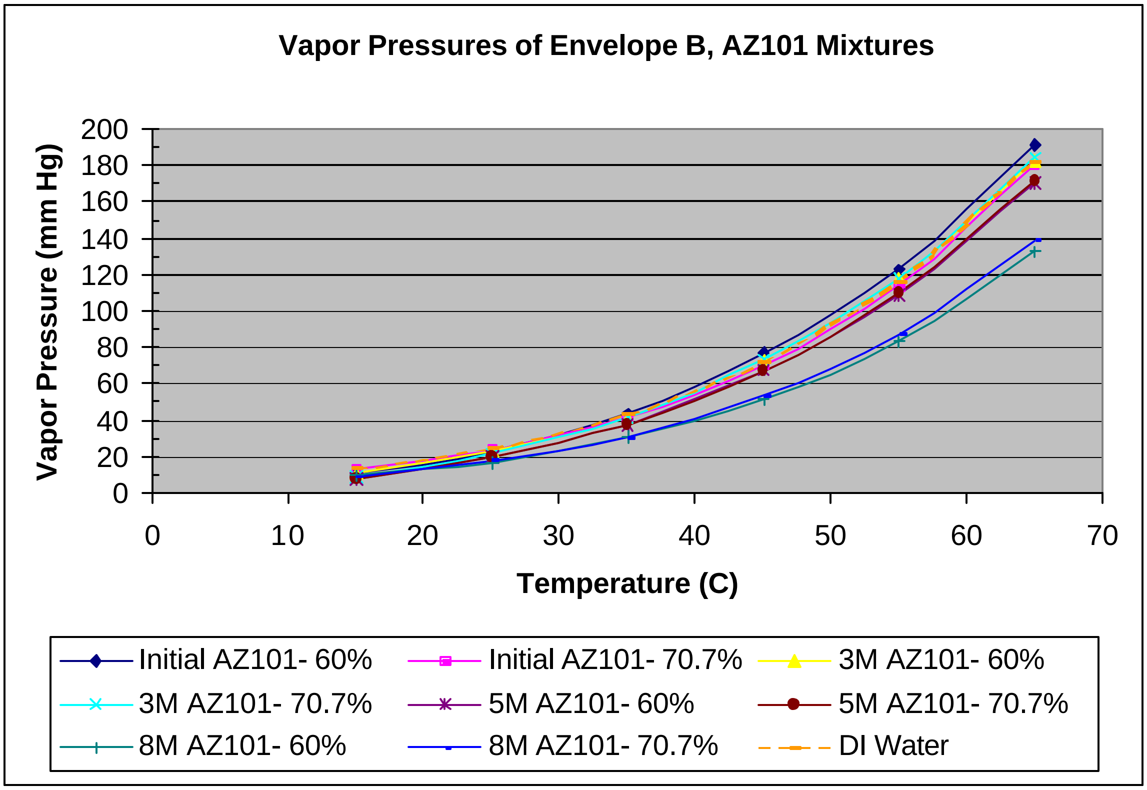

Figure A-13. Vapor Pressures of Envelope B AZ102 Mixtures

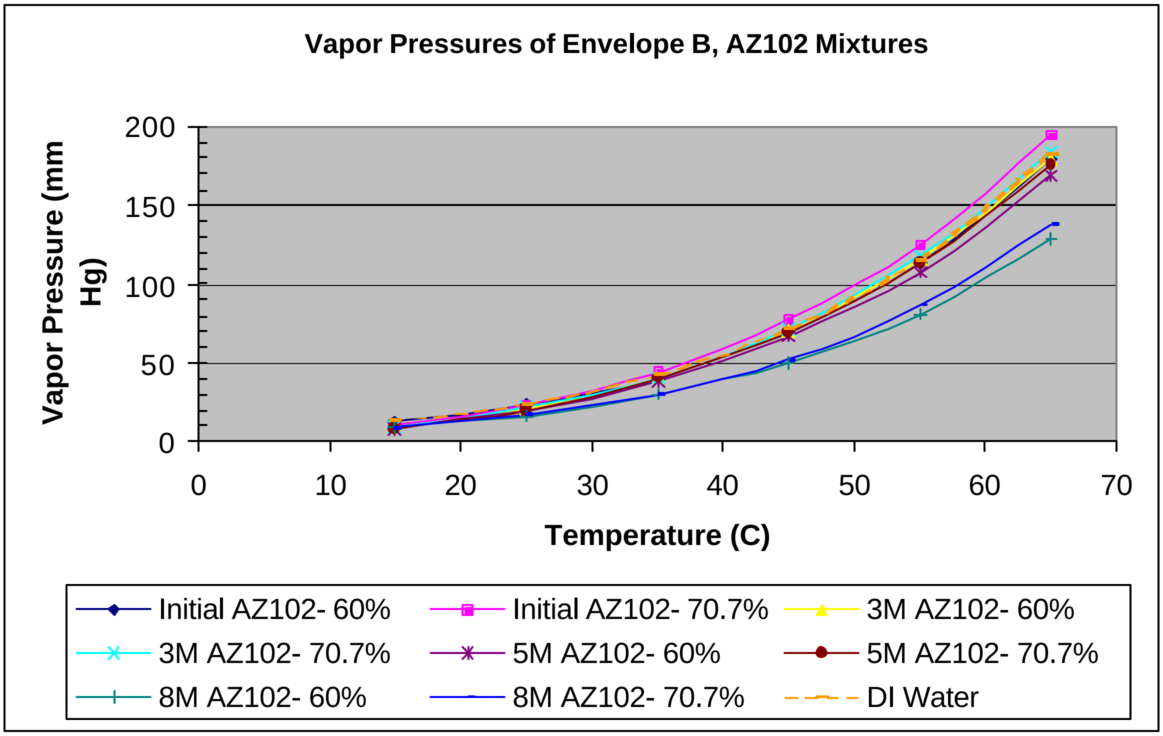

Figure A-14. Vapor Pressures of Envelope B AZ102 Mixtures

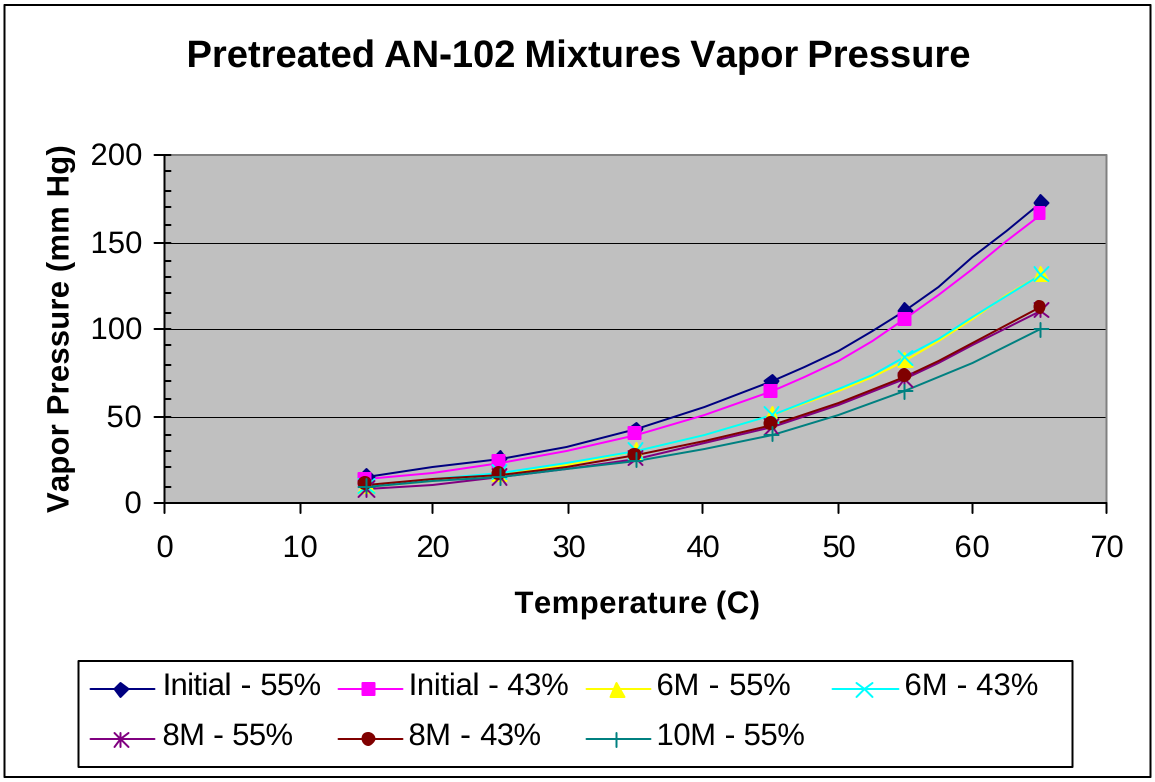

Figure A-15. Vapor Pressures of Envelope C AN102 Mixtures

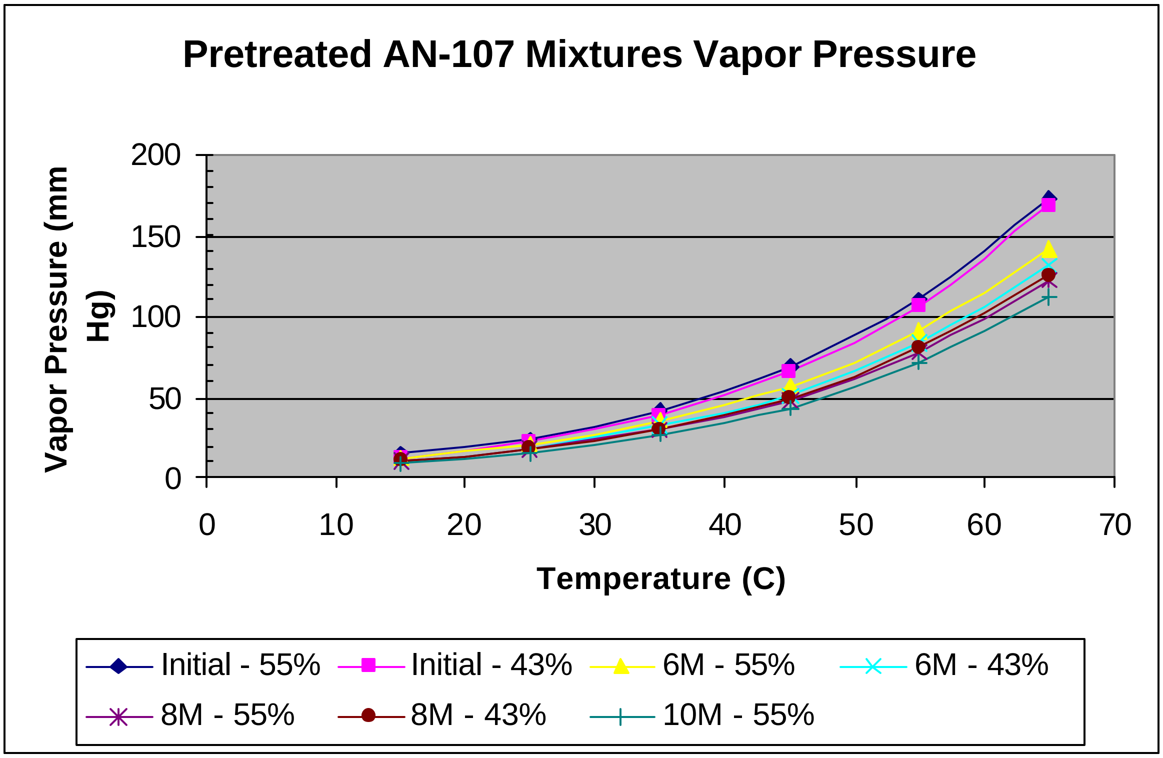

Figure A-16. Vapor Pressures of Envelope C AN107 Mixtures

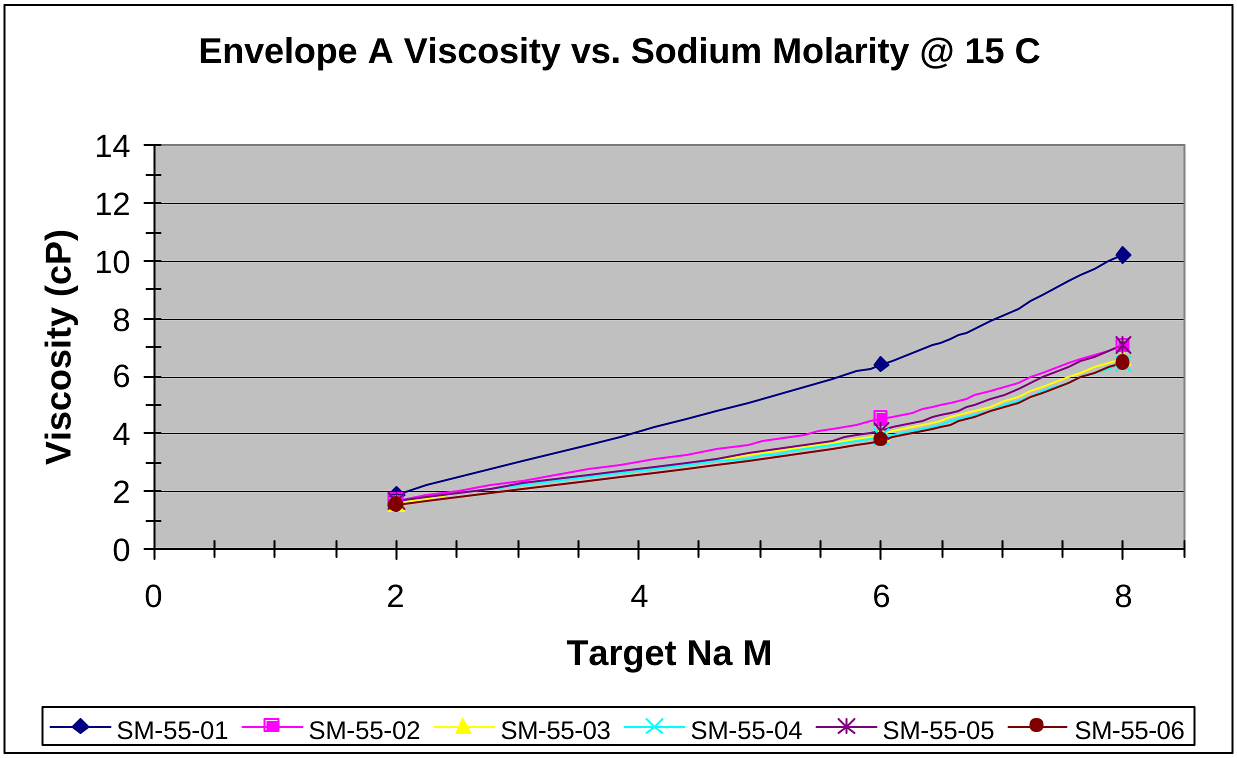

Figure A-17. Envelope A 1-6: Measured Viscosity vs. Na M @ 15 C

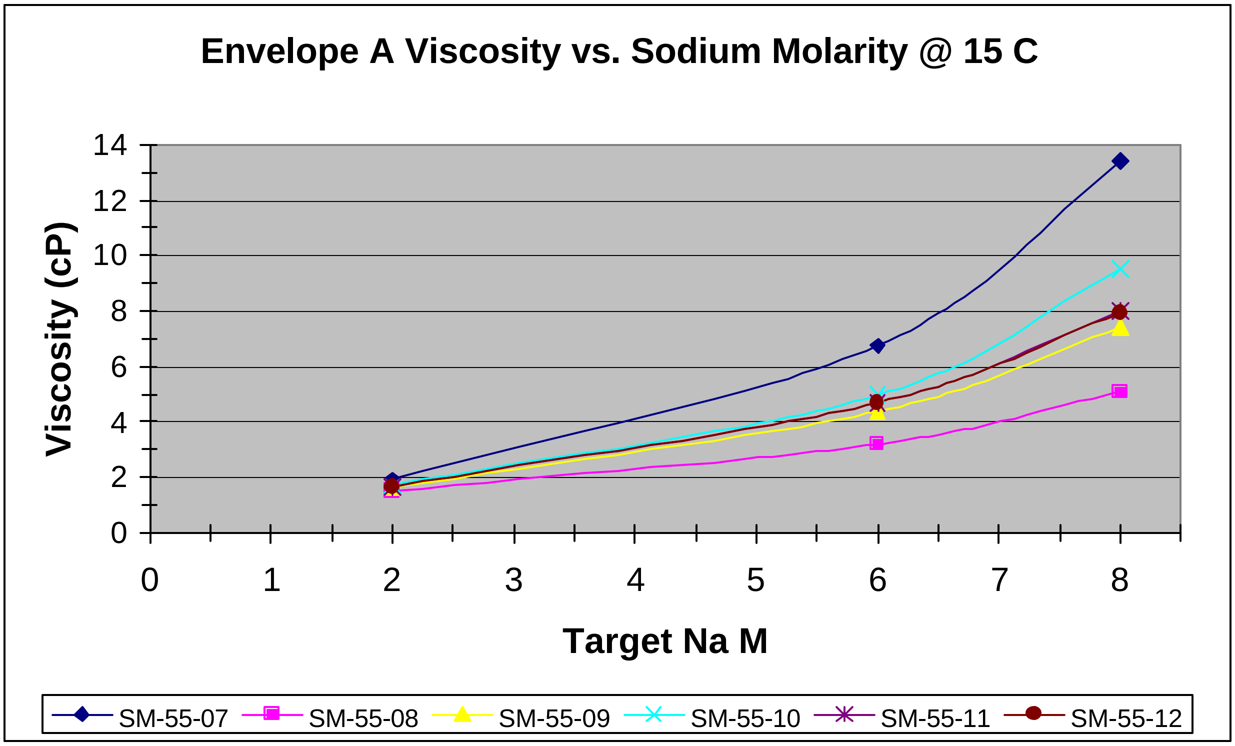

Figure A-18. Envelope A 7-12: Measured Viscosity vs. Na M @ 15 C

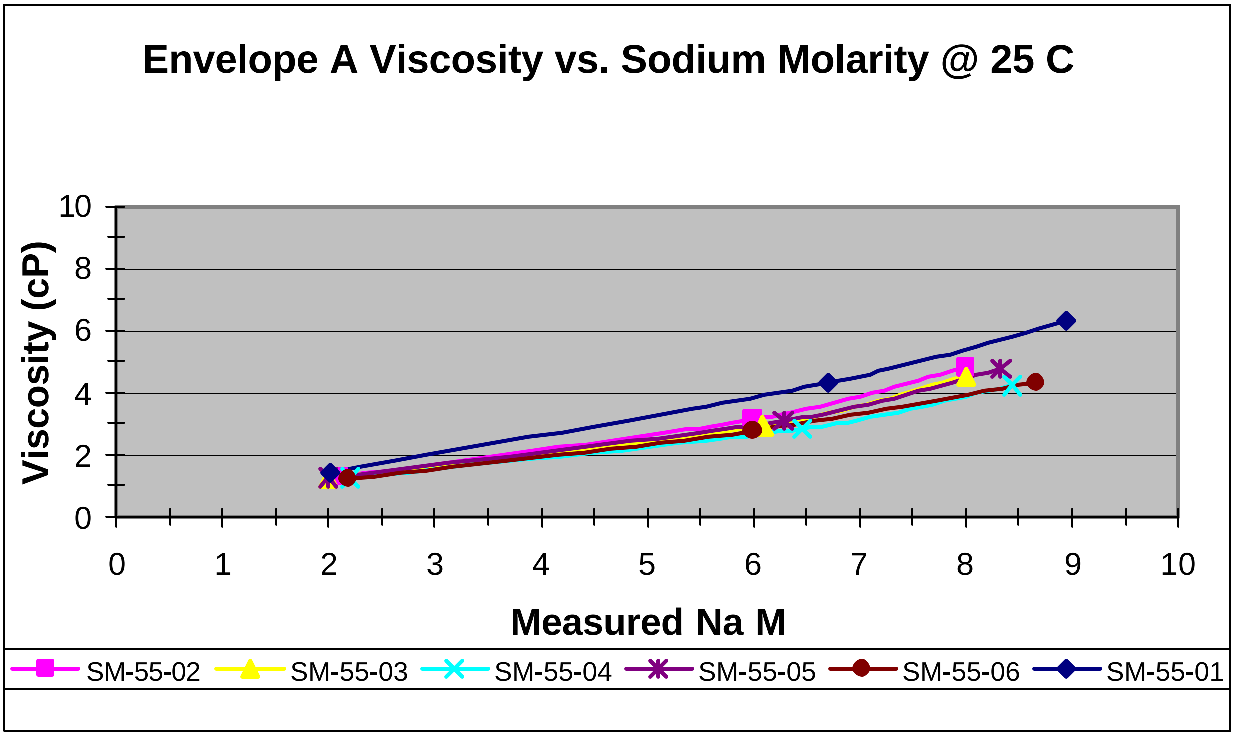

Figure A-19. Envelope A 1-6: Measured Viscosity vs. Na M @ 25 C

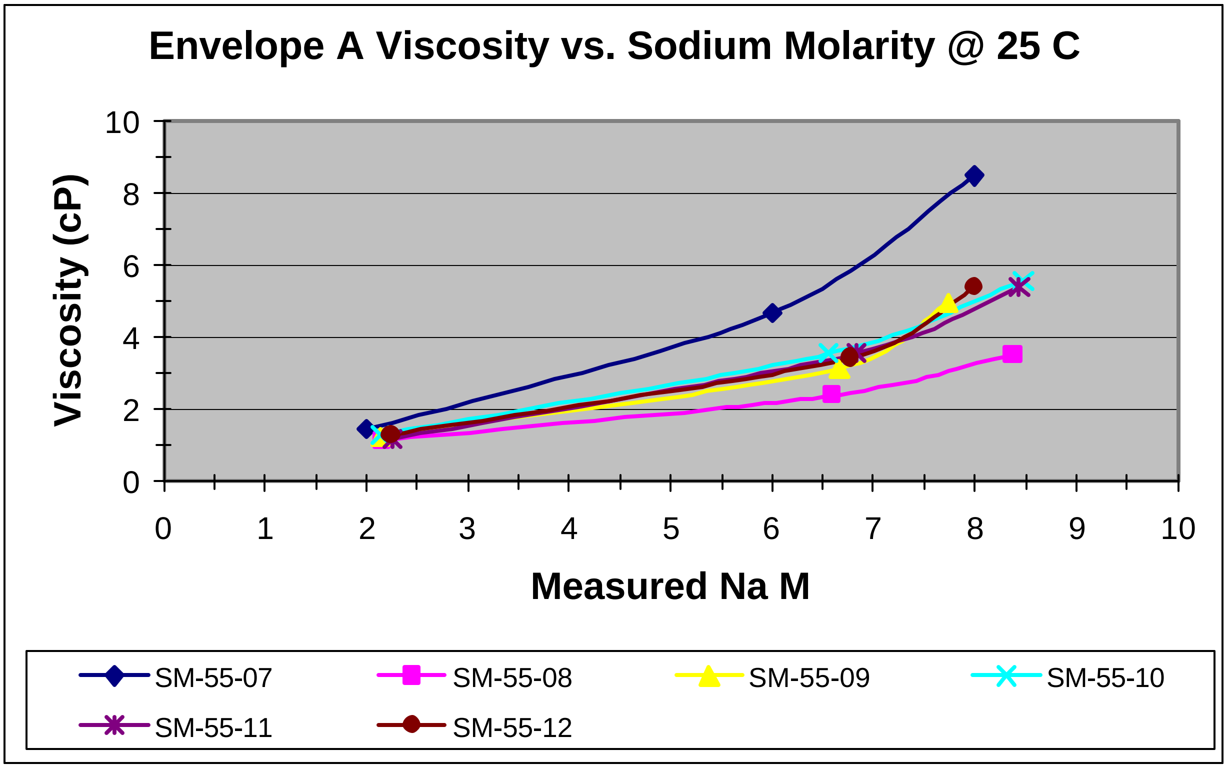

Figure A-20. Envelope A 7-12: Measured Viscosity vs. Na M @ 25 C

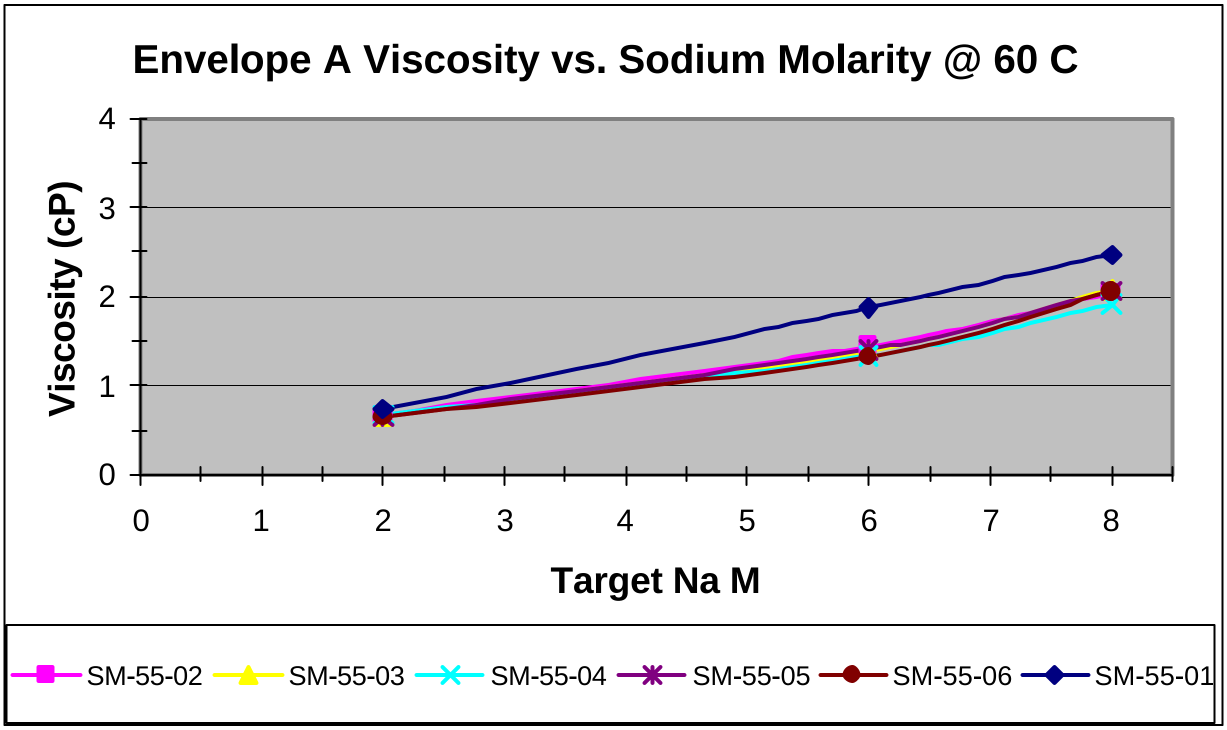

Figure A-21. Envelope A 1-6: Measured Viscosity vs. Na M @ 60 C

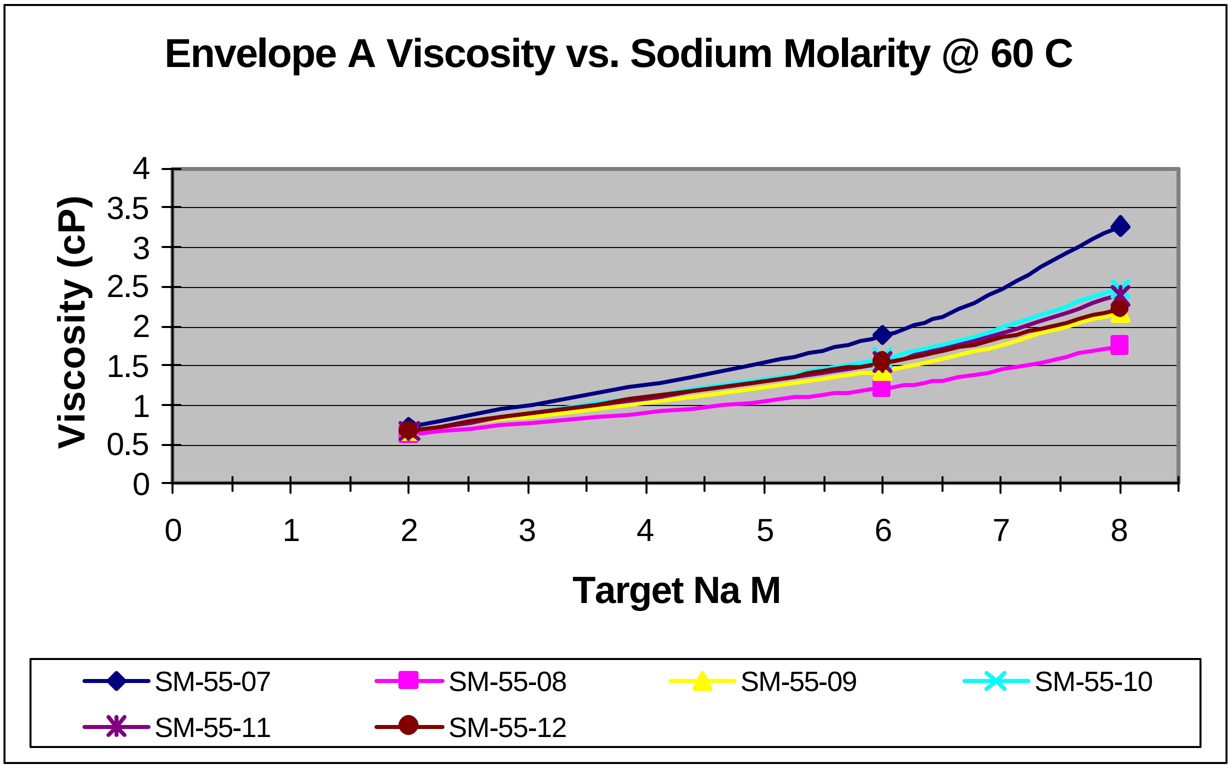

Figure A-22. SM-55-07 to SM-55-12: Measured Viscosity vs. Na M @ 60 C

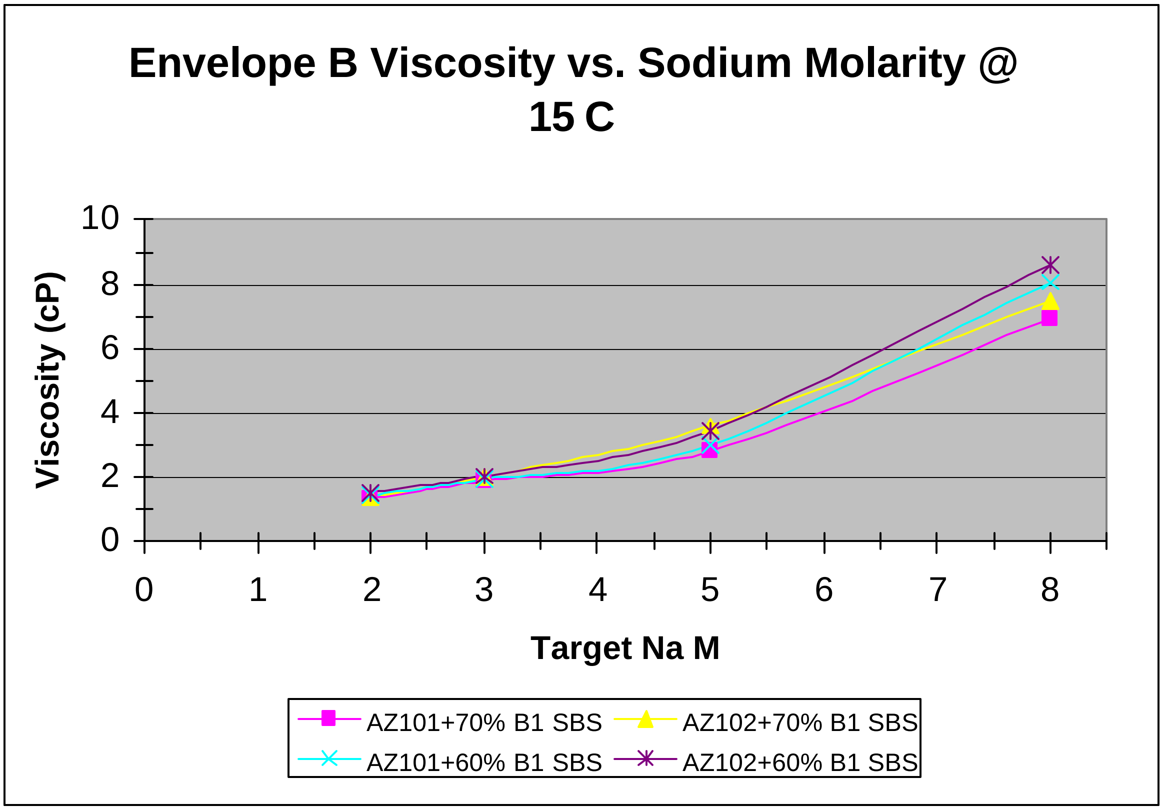

Figure A-23. Envelope B: Measured Viscosity vs. Na M @ 15 C

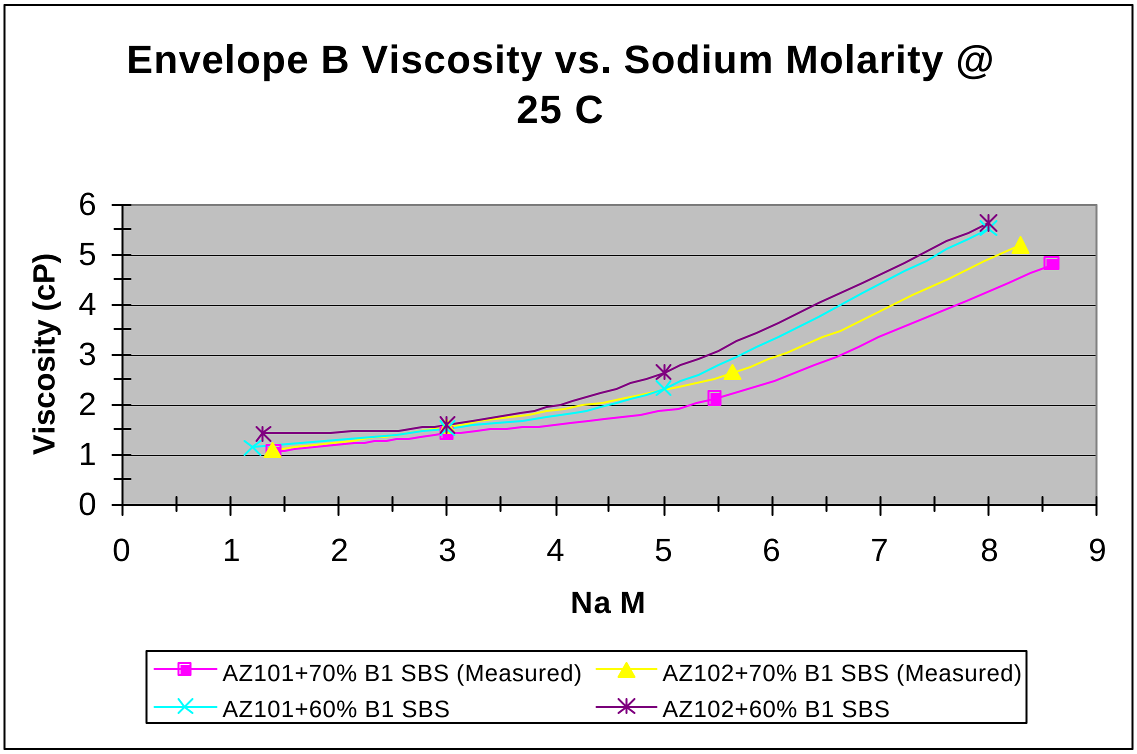

Figure A-24. Envelope B: Measured Viscosity vs. Na M @ 25 C

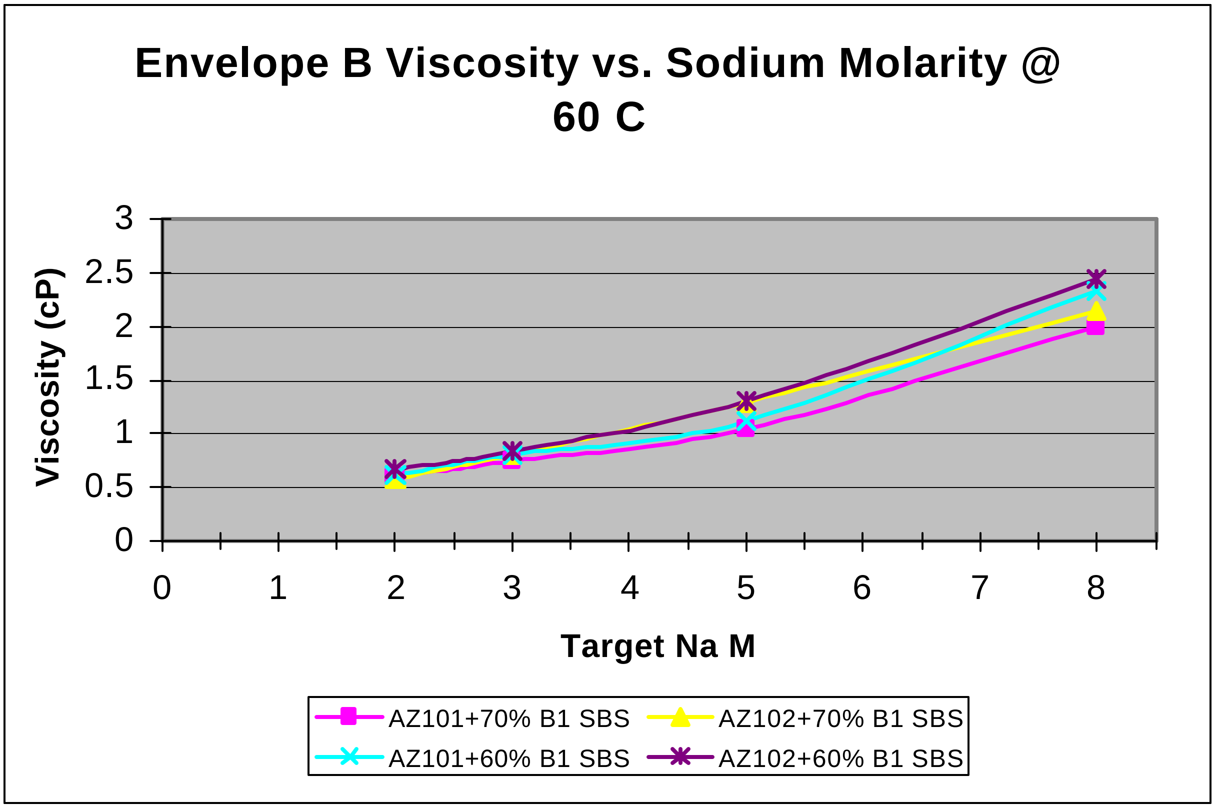

Figure A-25. Envelope B: Measured Viscosity vs. Na M @ 60 C

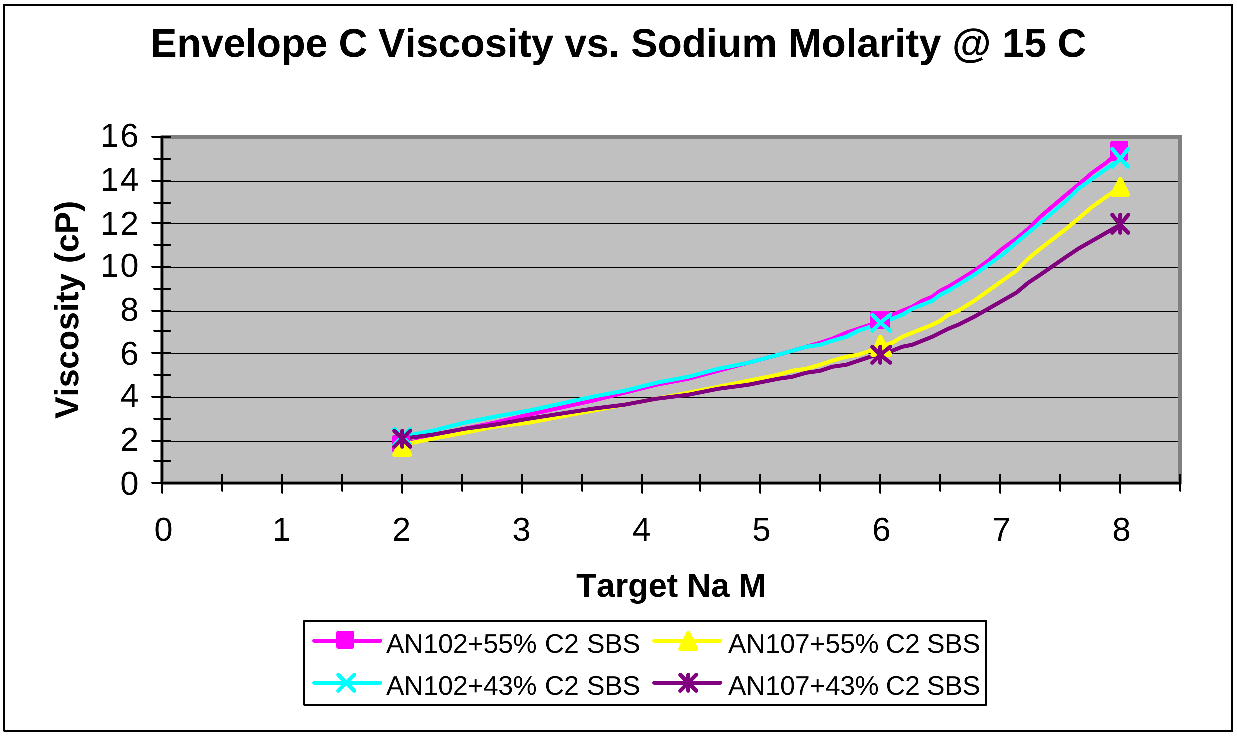

Figure A-26. Envelope C: Measured Viscosity vs. Na M @ 15 C

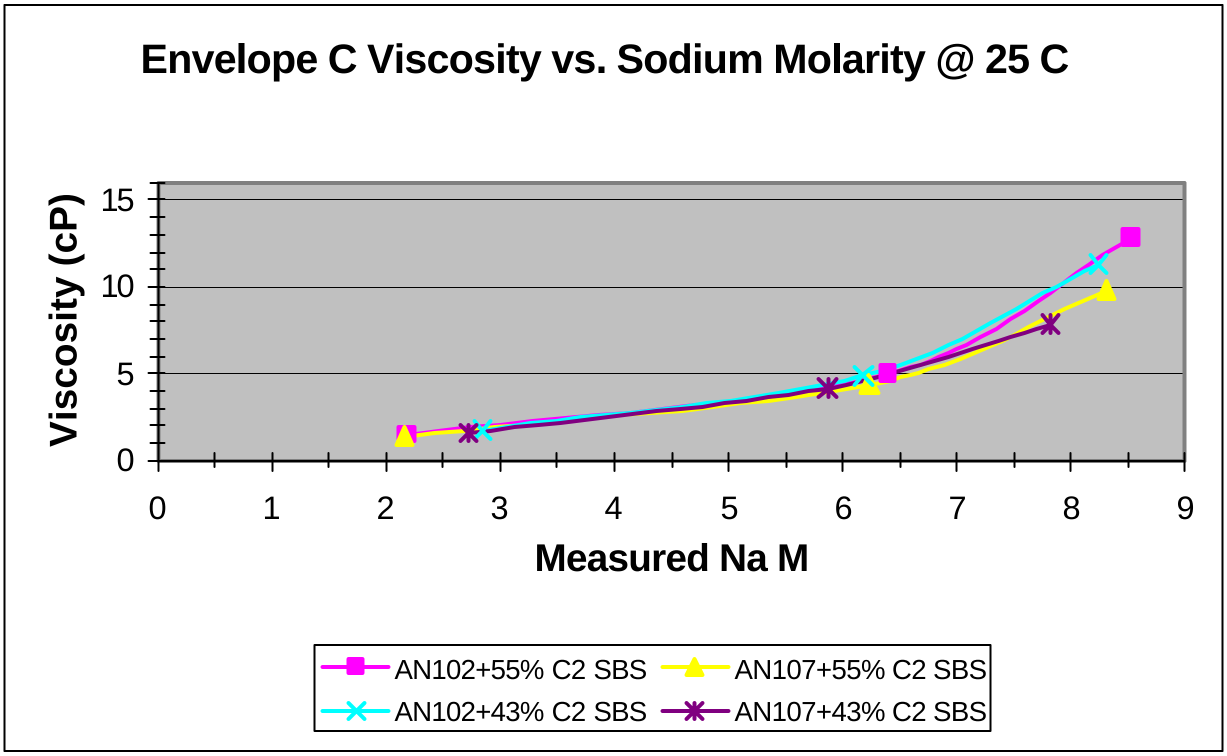

Figure A-27. Envelope C: Measured Viscosity vs. Na M @ 25 C

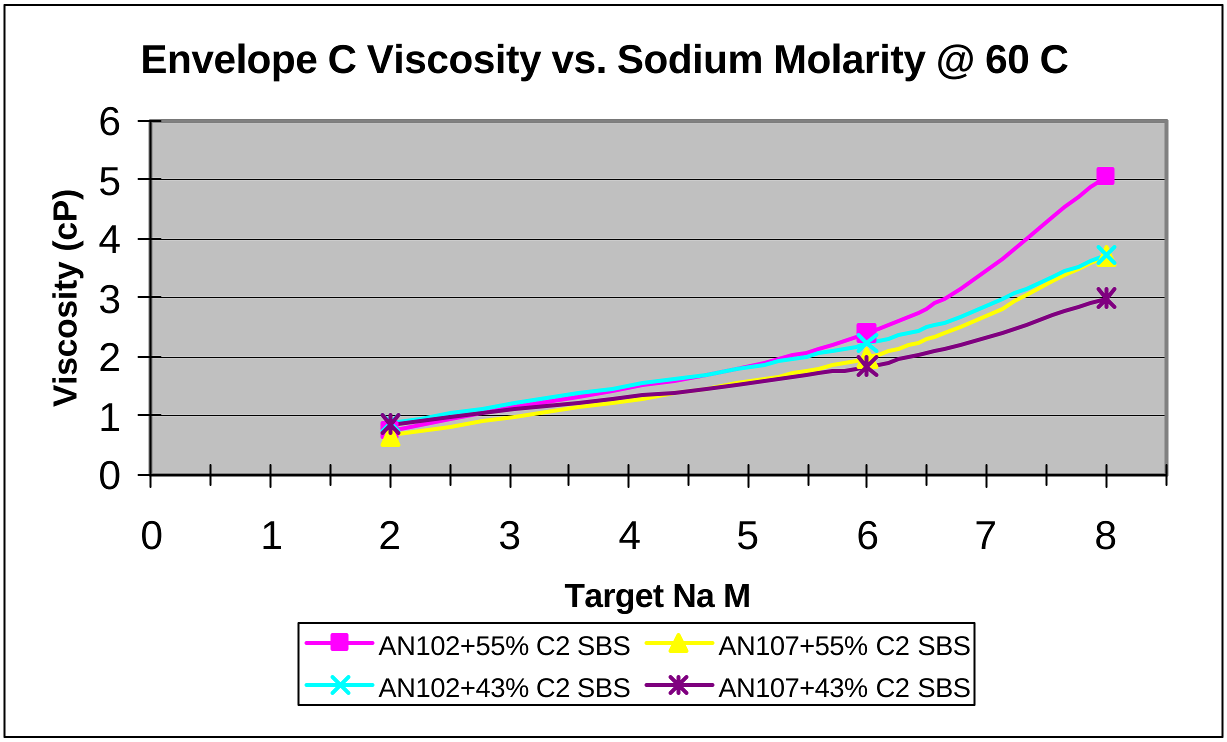

Figure A-28. Envelope C: Measured Viscosity vs. Na M @ 60 C

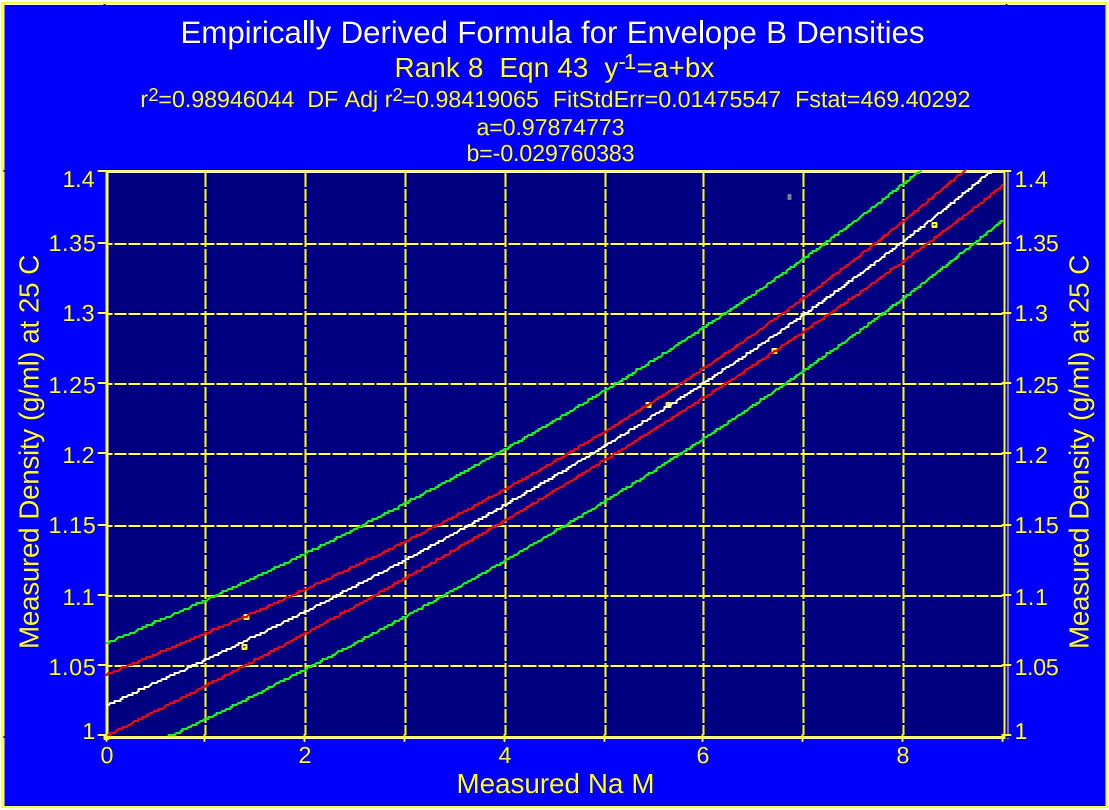

Figure A-29. Empirical Formula for Envelope B Density Trend

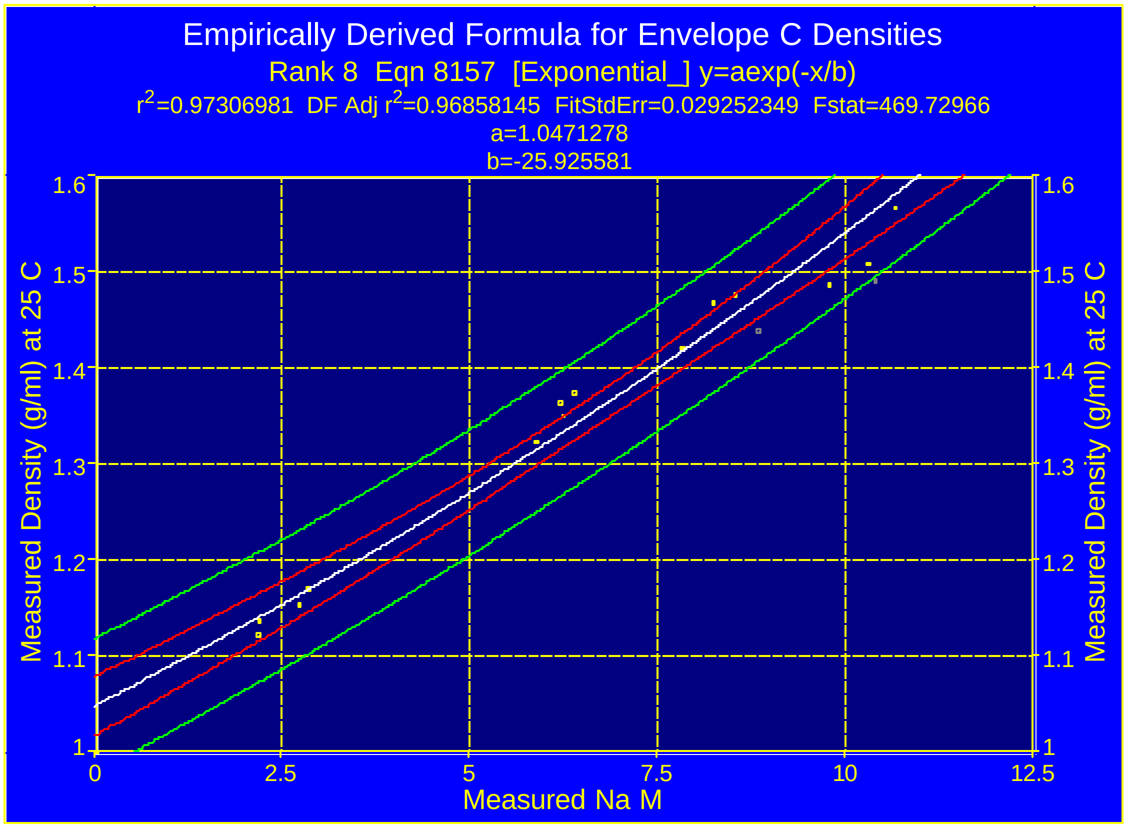

Figure A-30. Empirical Formula for Envelope C Density Trend

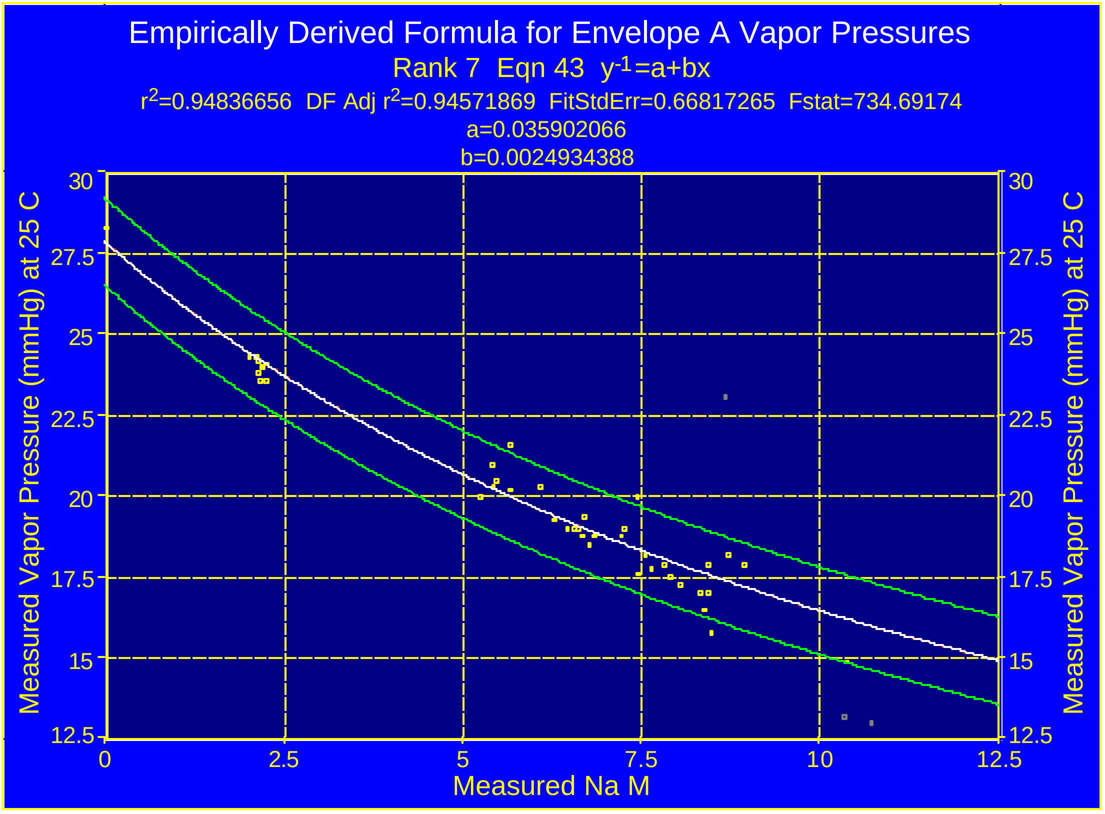

Figure A-31. Empirical Formula for Envelope A Vapor Pressure Trend

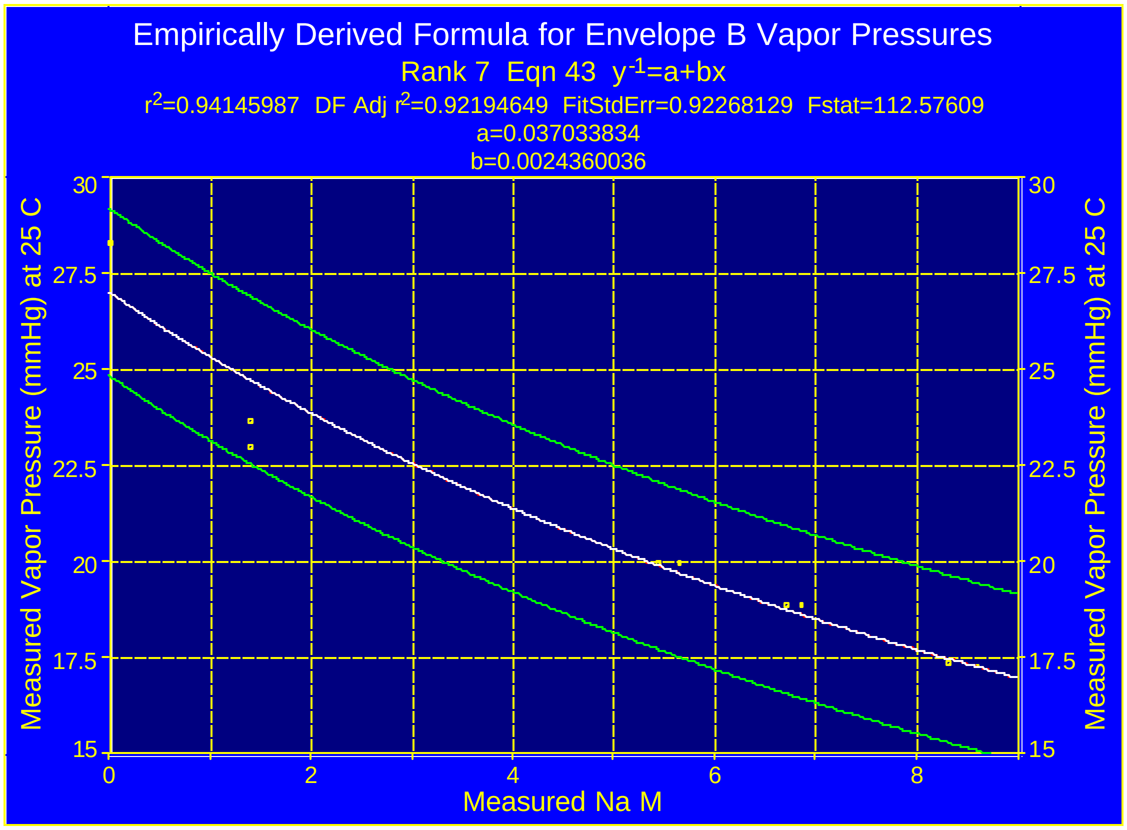

Figure A-32. Empirical Formula for Envelope B Vapor Pressure Trend

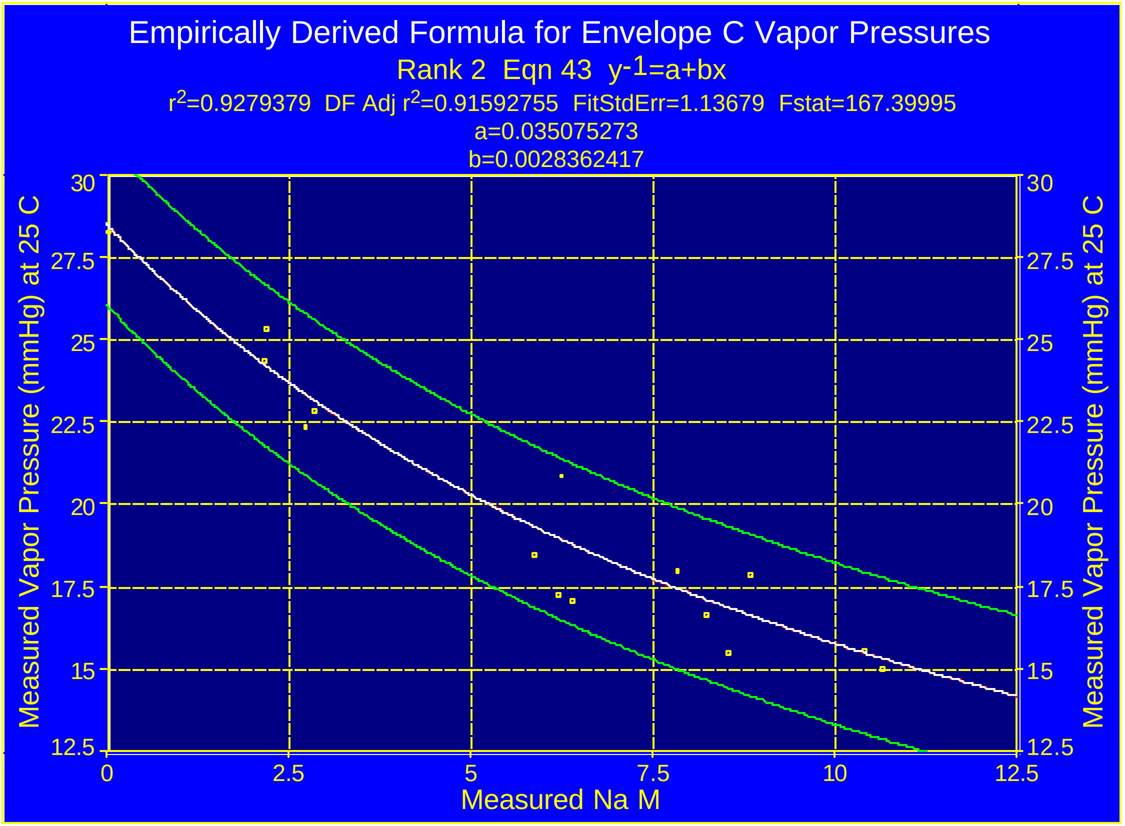

Figure A-33. Empirical Formula for Envelope C Vapor Pressure Trend

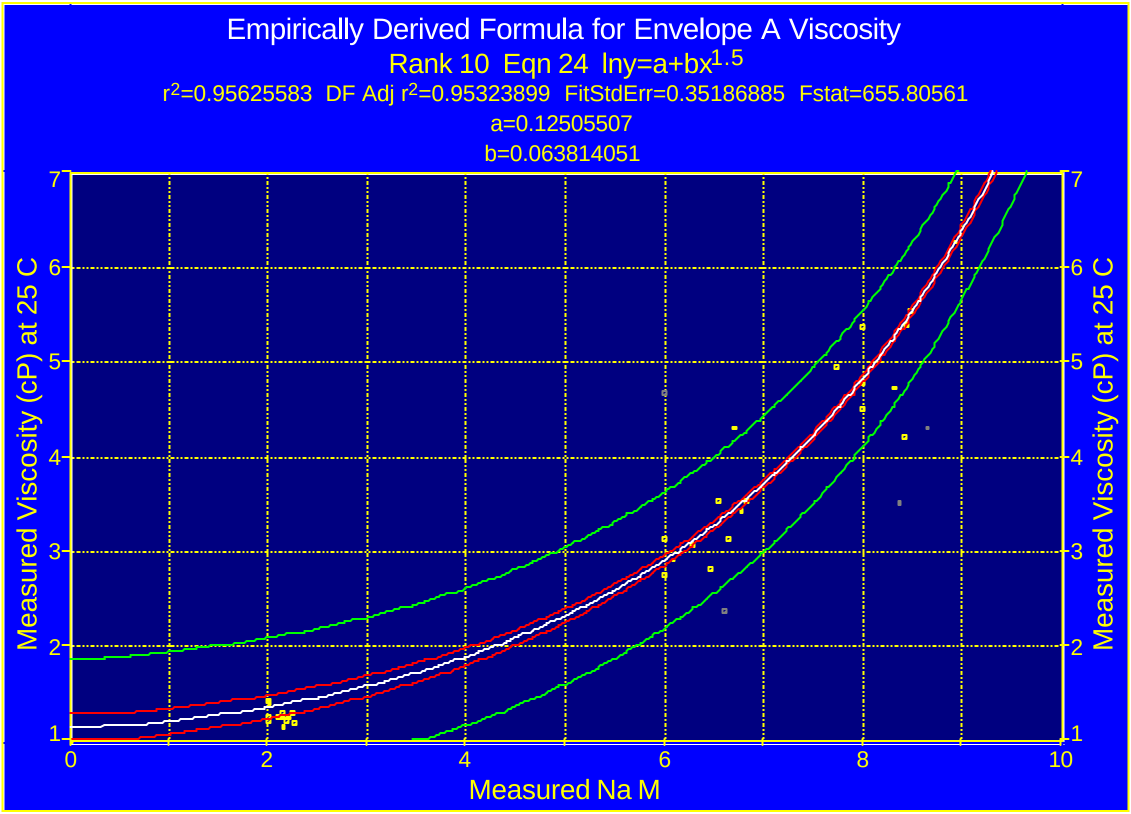

Figure A-34. Empirical Formula for Envelope A Viscosity Trend

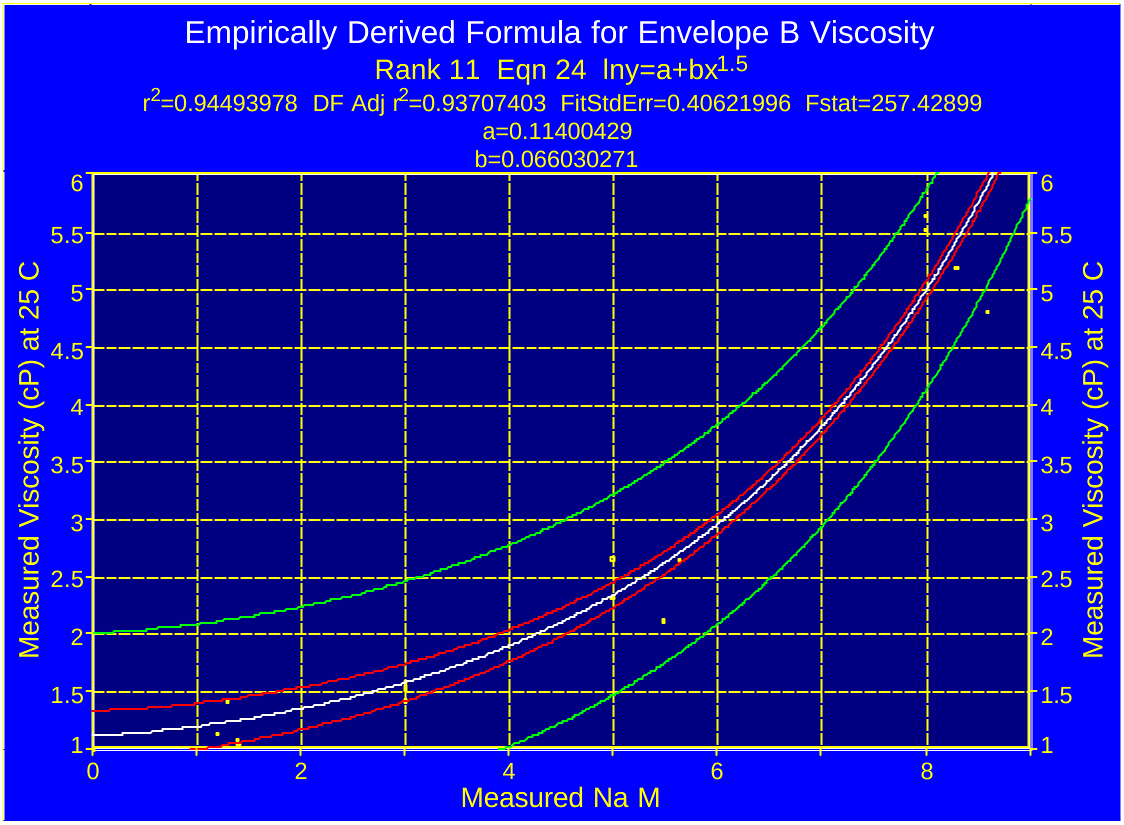

Figure A-35. Empirical Formula for Envelope B Viscosity Trend

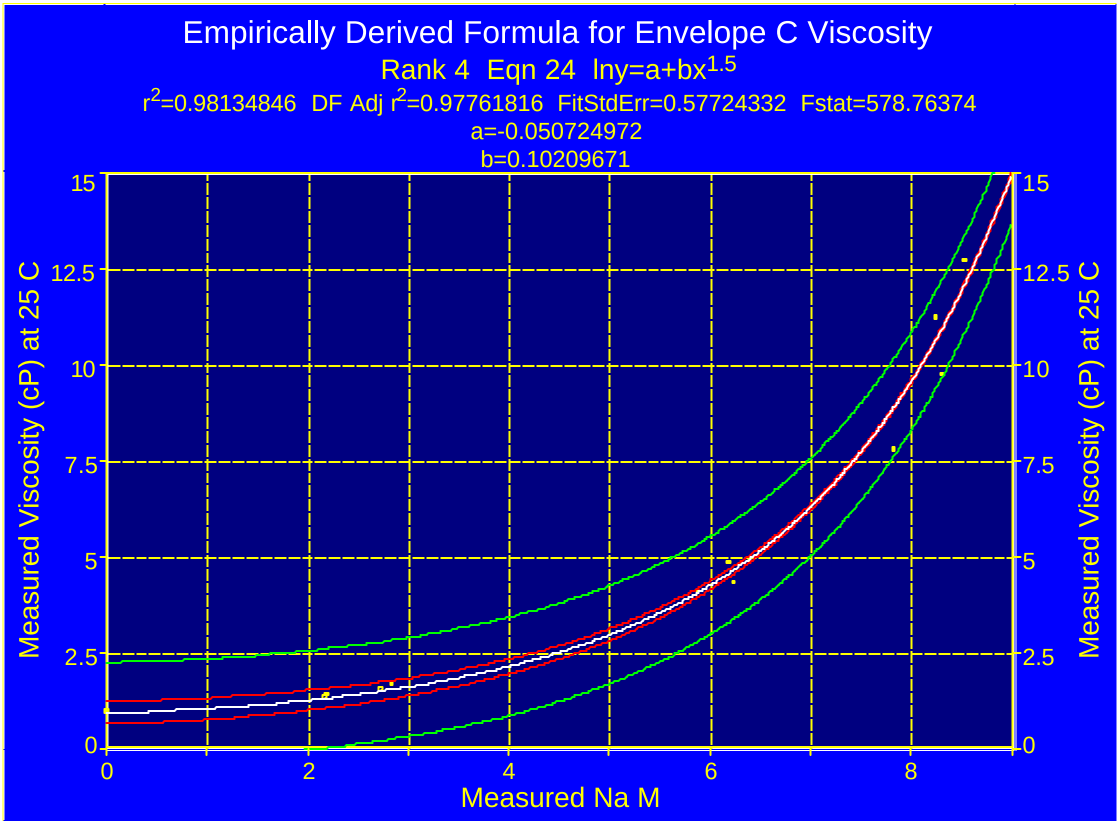

Figure A-36. Empirical Formula for Envelope C Viscosity Trend

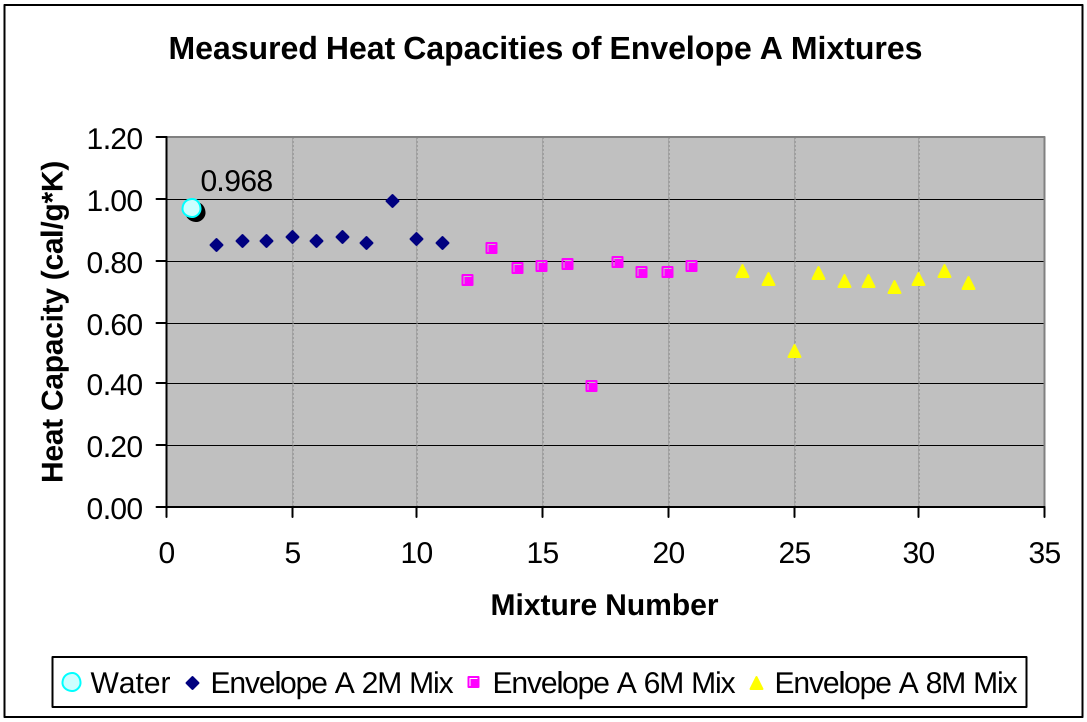

Figure A-37. Heat Capacities of Envelope A Mixtures

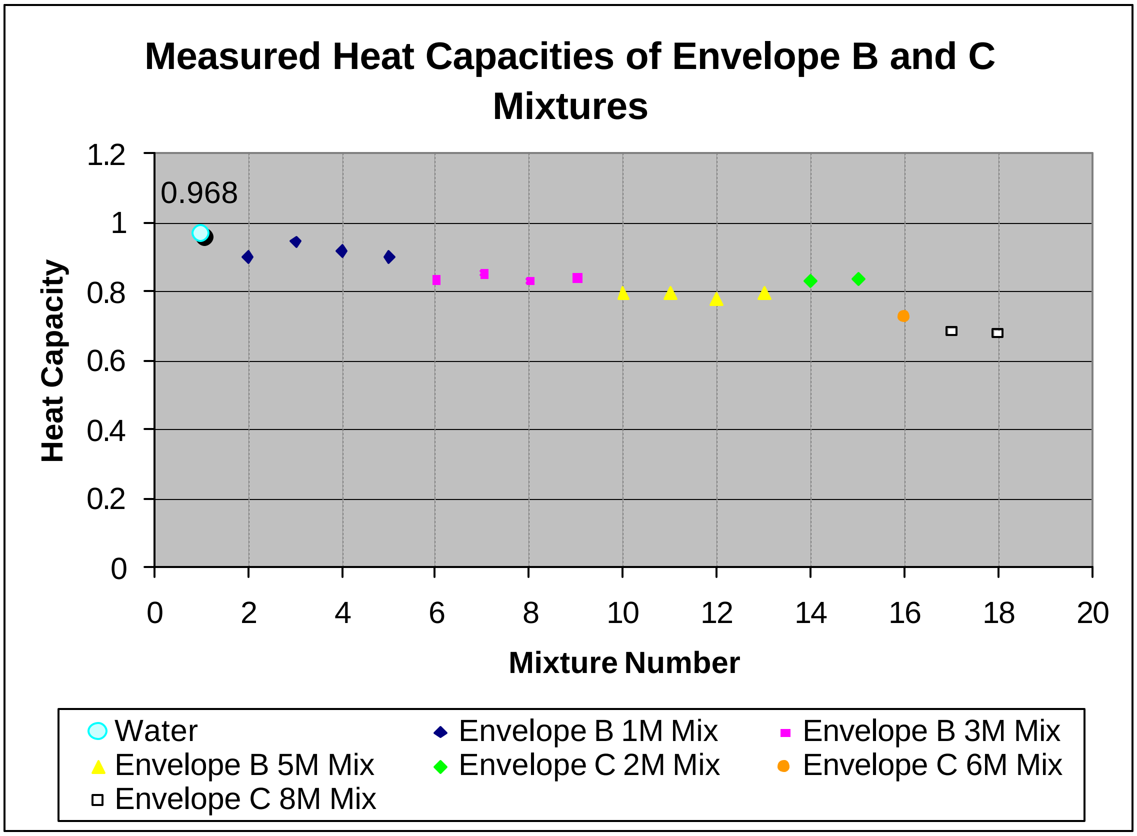

Figure A-38. Heat Capacities of Envelope B & C Mixtures

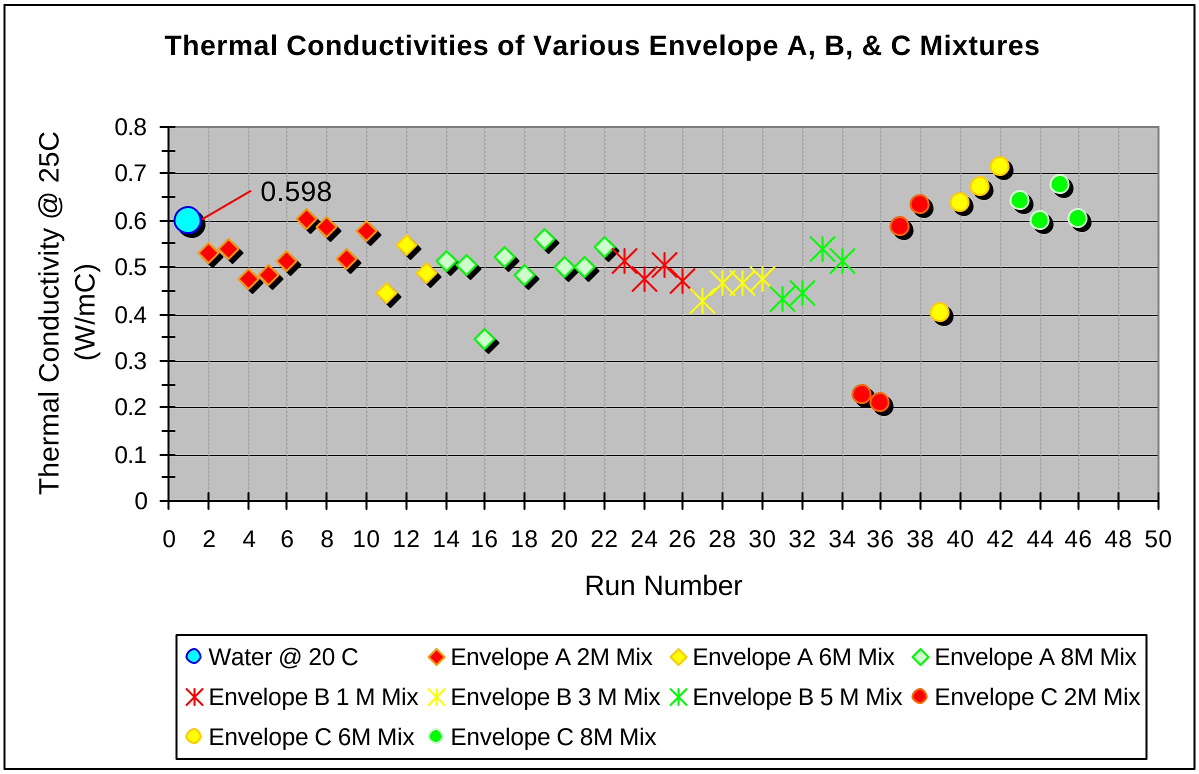

Figure A-39. Thermal Conductivities of Envelope A and C Mixtures

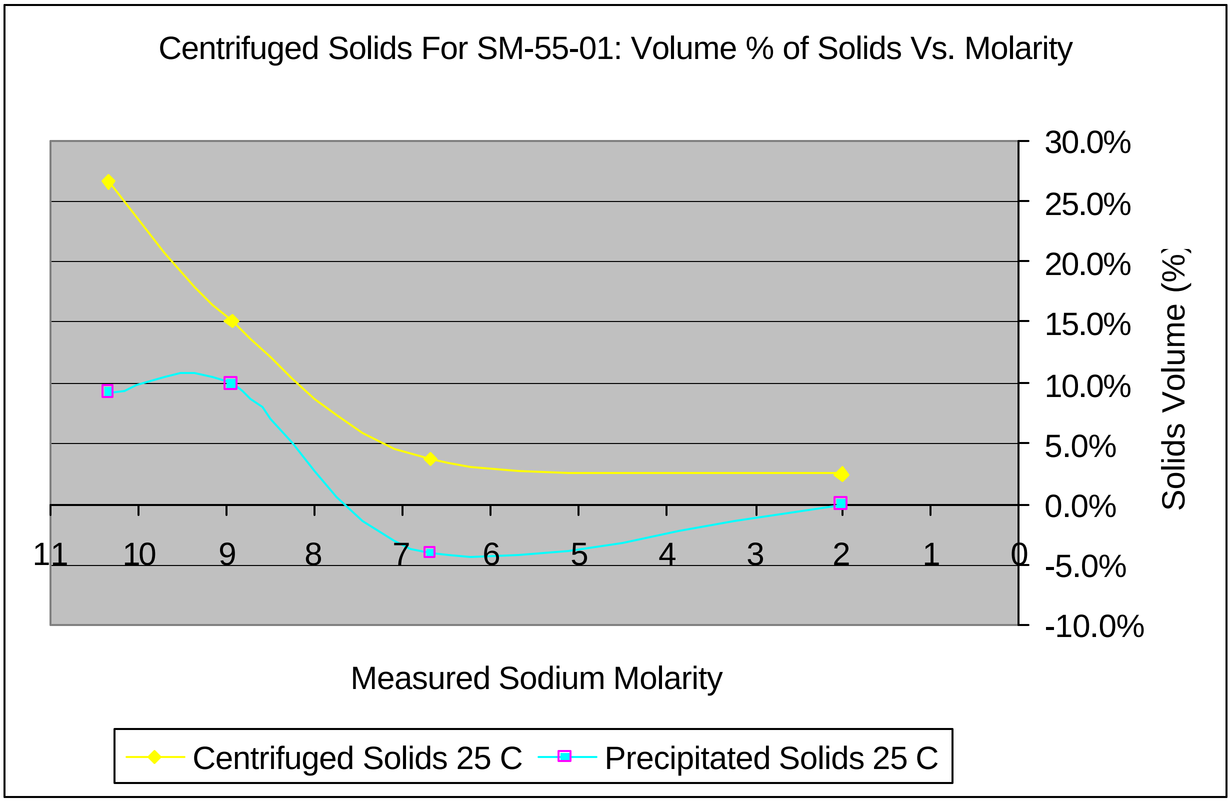

Figure A-40. Solids Volume % of Envelope A Mixture SM-55-01

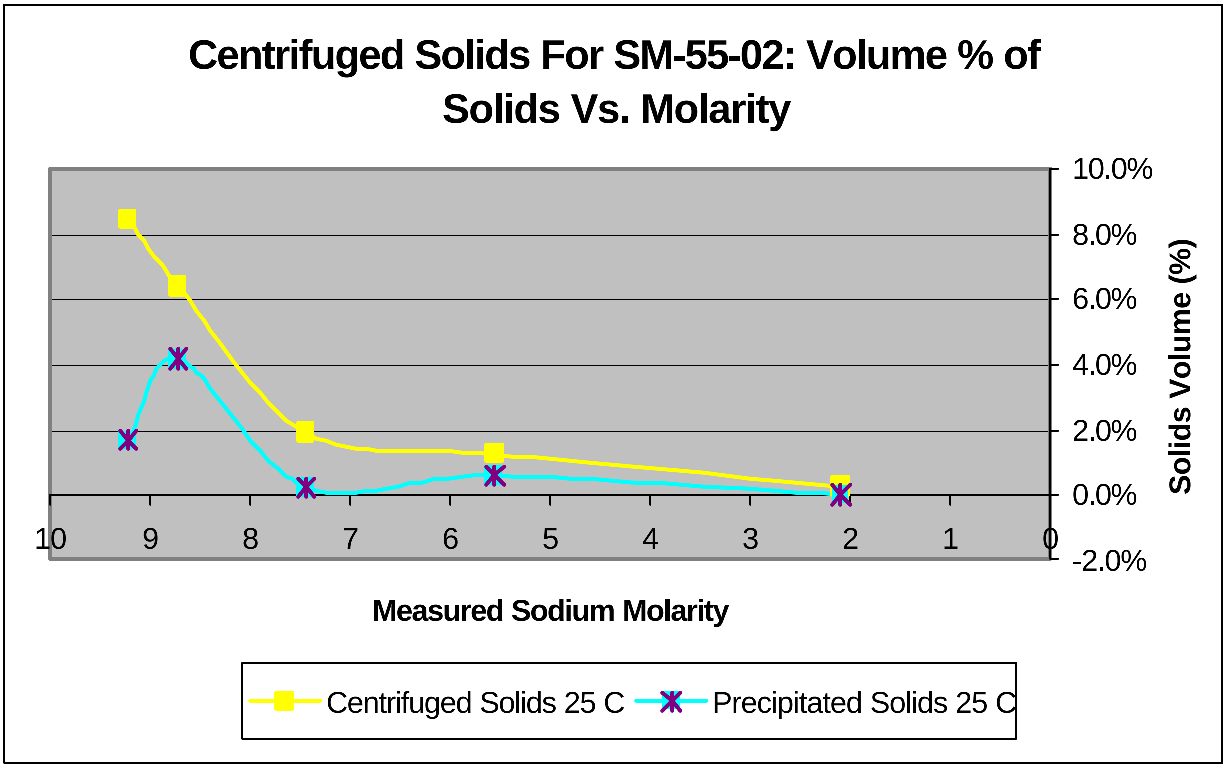

Figure A-41. Solids Volume % of Envelope A Mixture SM-55-02

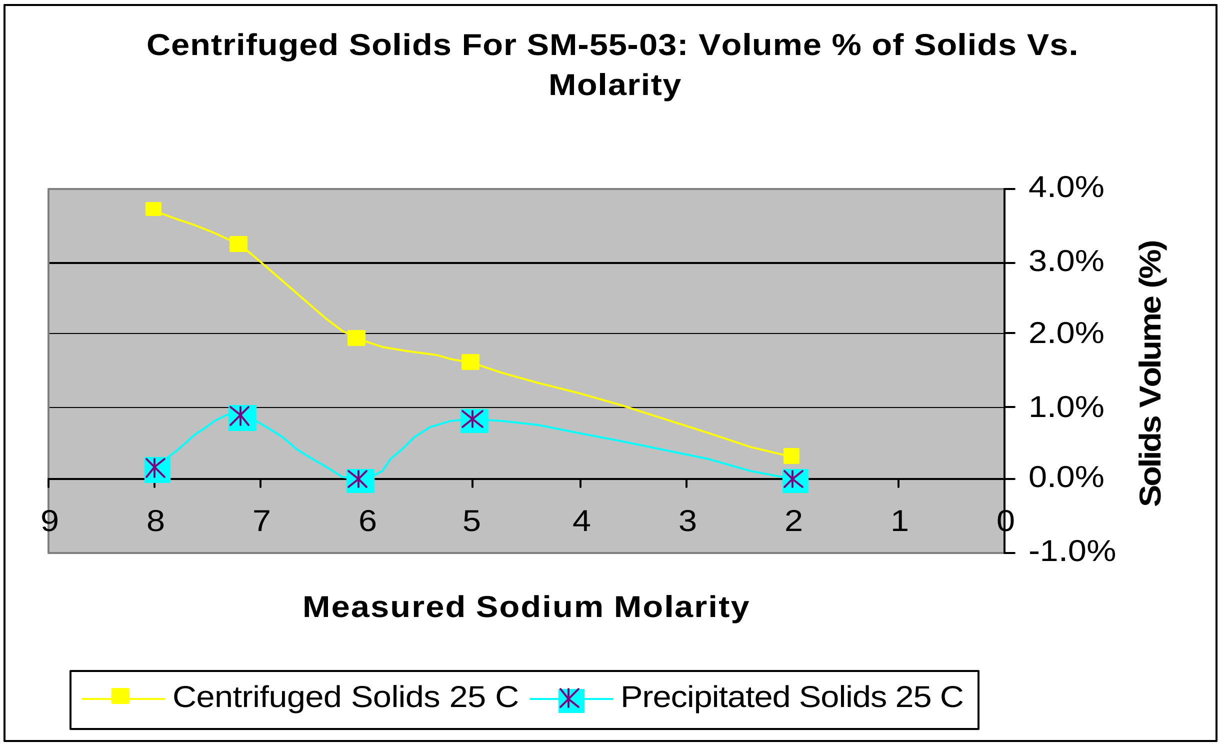

Figure A-42. Solids Volume % of Envelope A Mixture SM-55-03

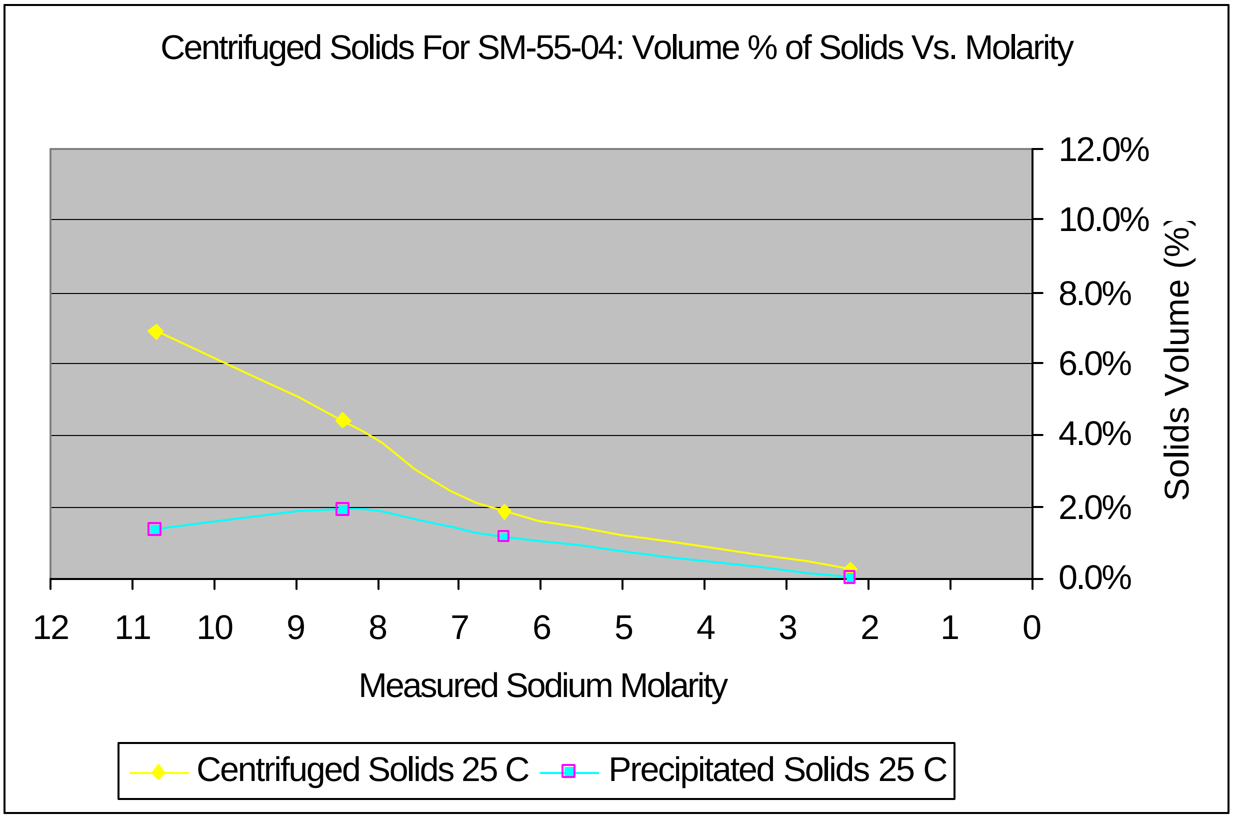

Figure A-43. Solids Volume % of Envelope A Mixture SM-55-04

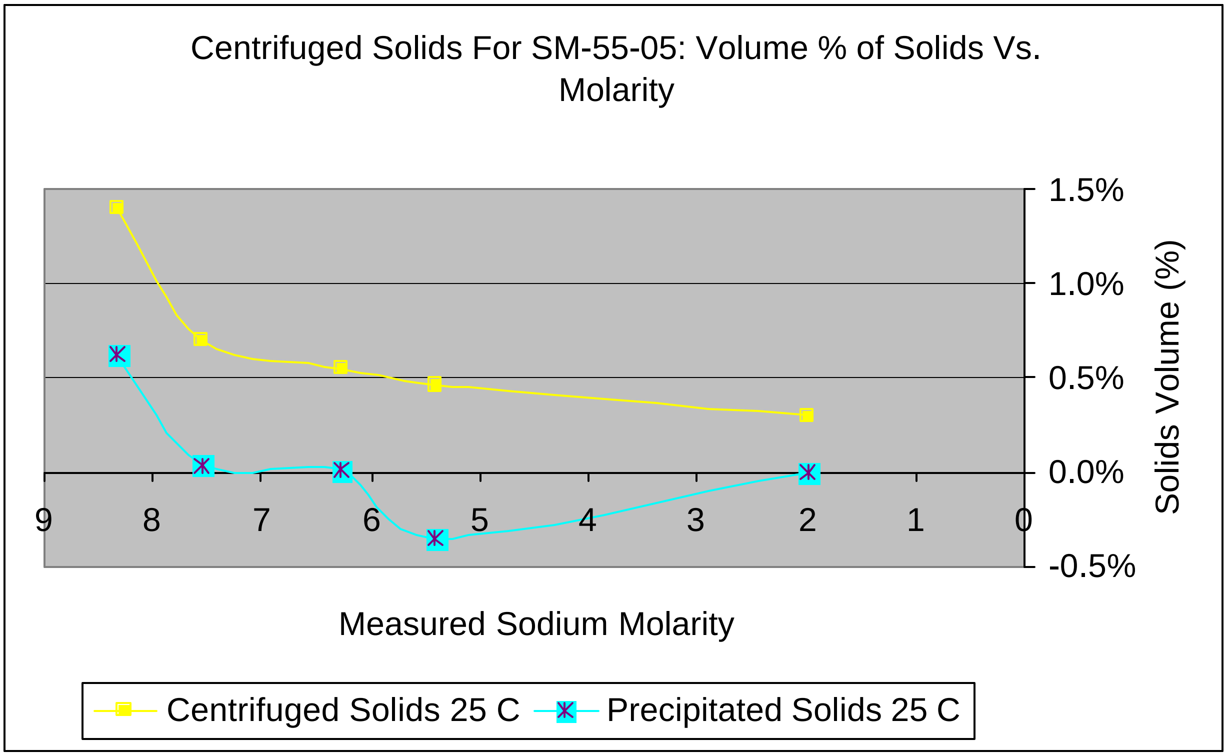

Figure A-44. Solids Volume % of Envelope A Mixture SM-55-05

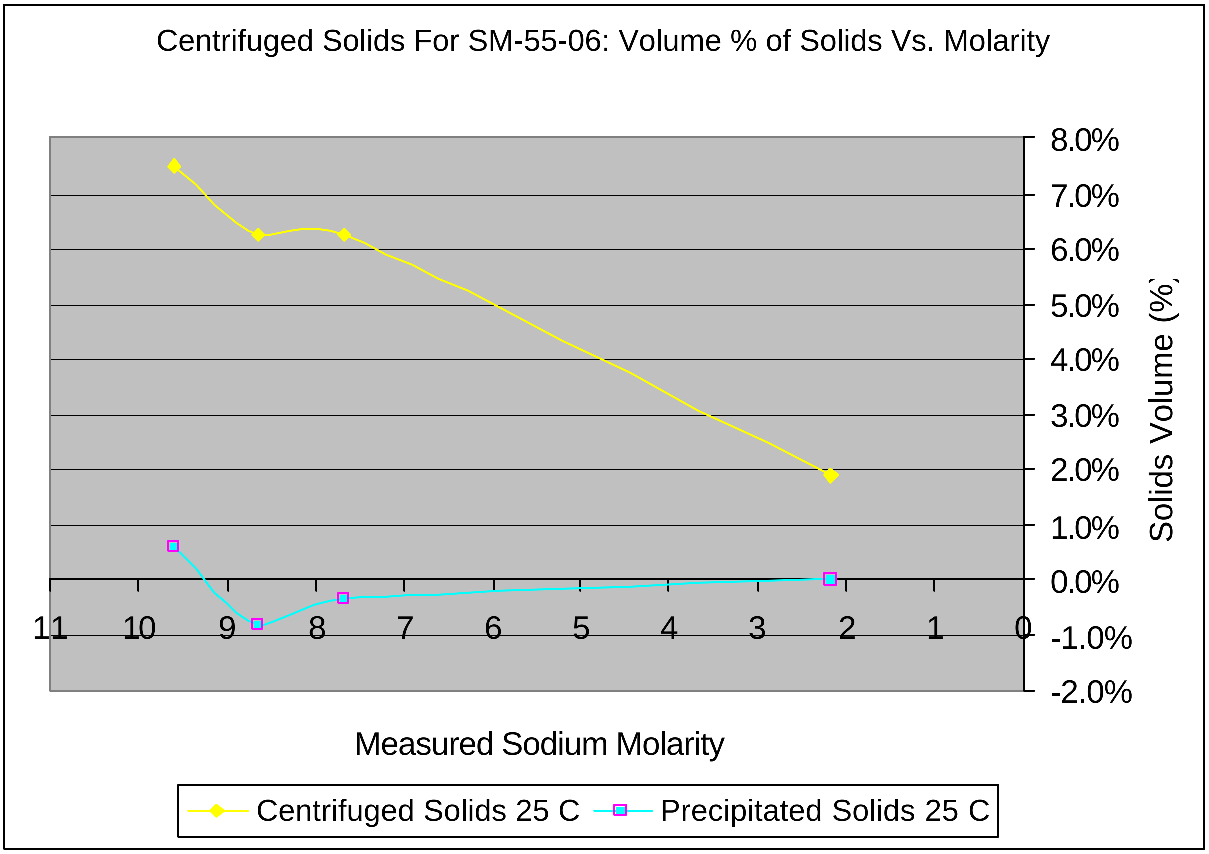

Figure A-45. Solids Volume % of Envelope A Mixture SM-55-06

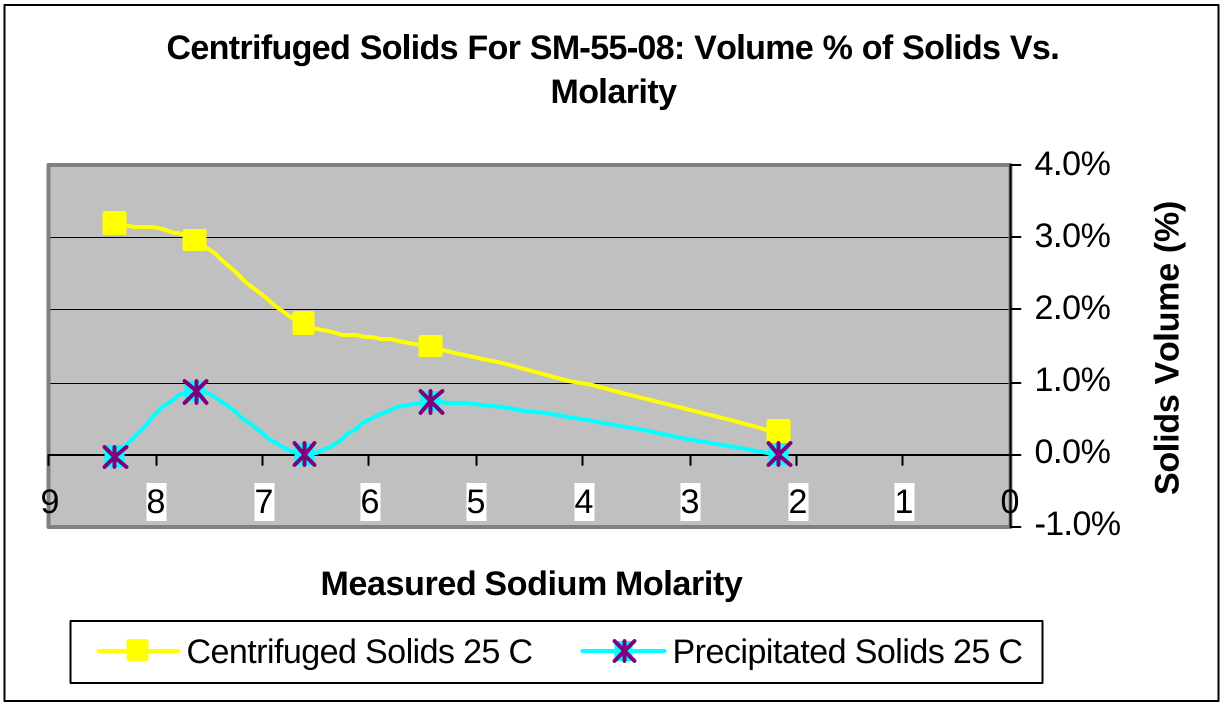

Figure A-46. Solids Volume % of Envelope A Mixture SM-55-08

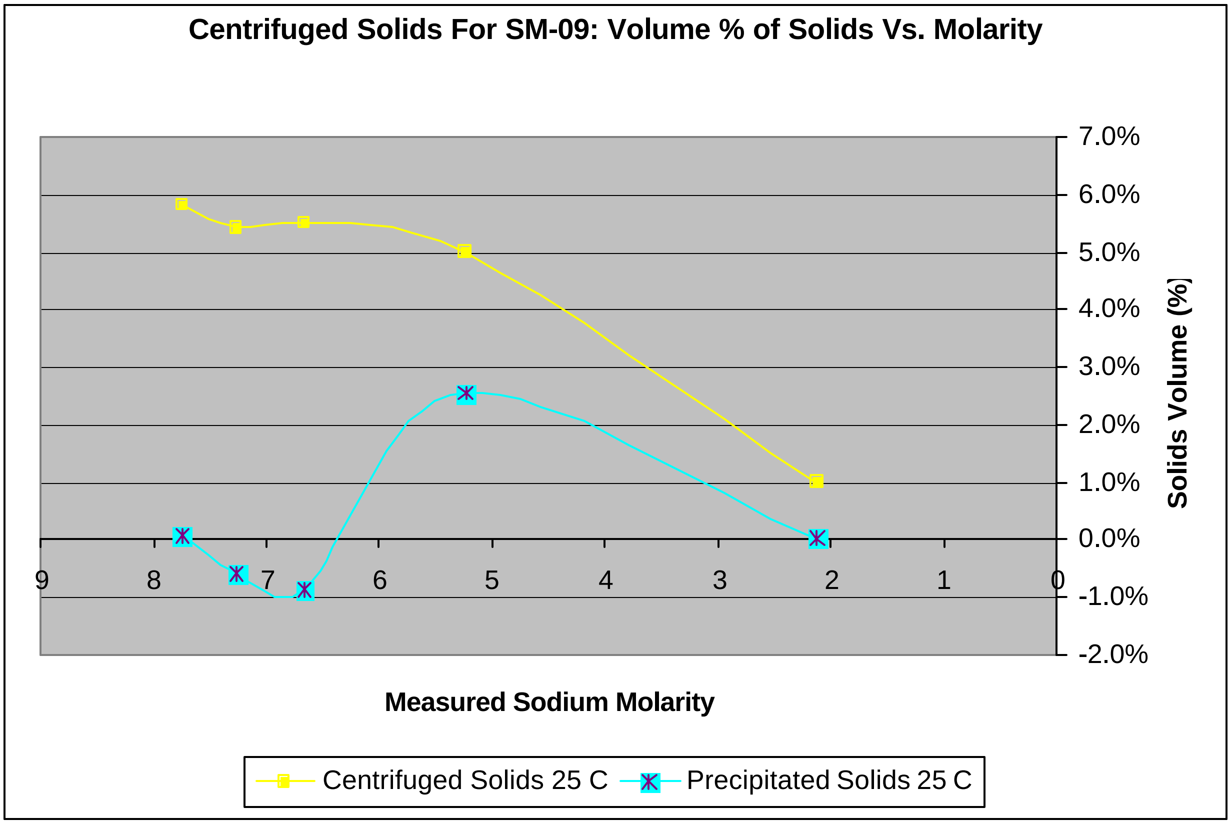

Figure A-47. Solids Volume % of Envelope A Mixture SM-55-09

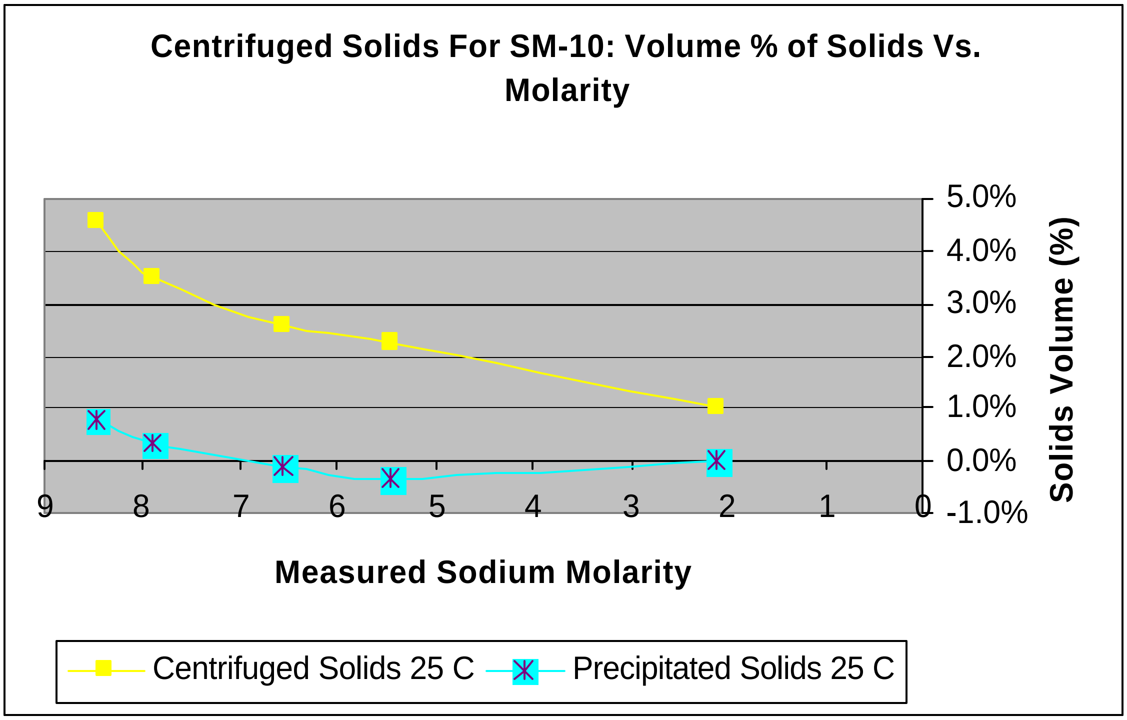

Figure A-48. Solids Volume % of Envelope A Mixture SM-55-10

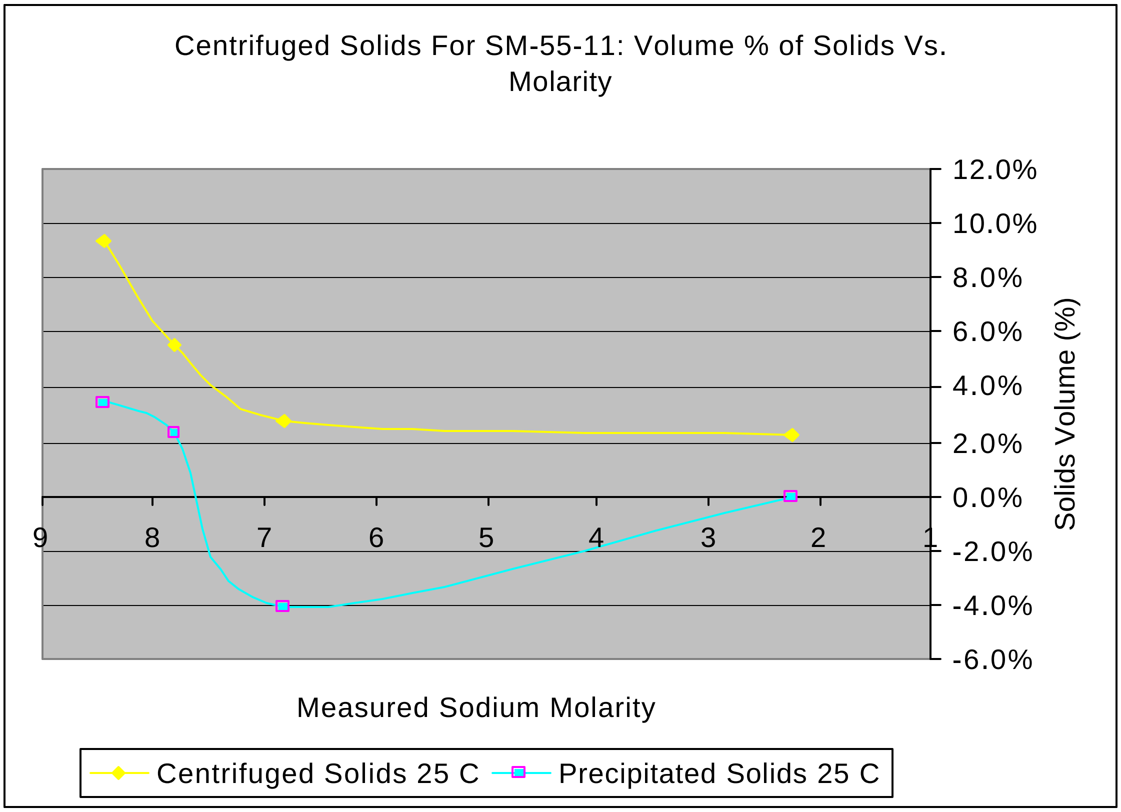

Figure A-49. Solids Volume % of Envelope A Mixture SM-55-11

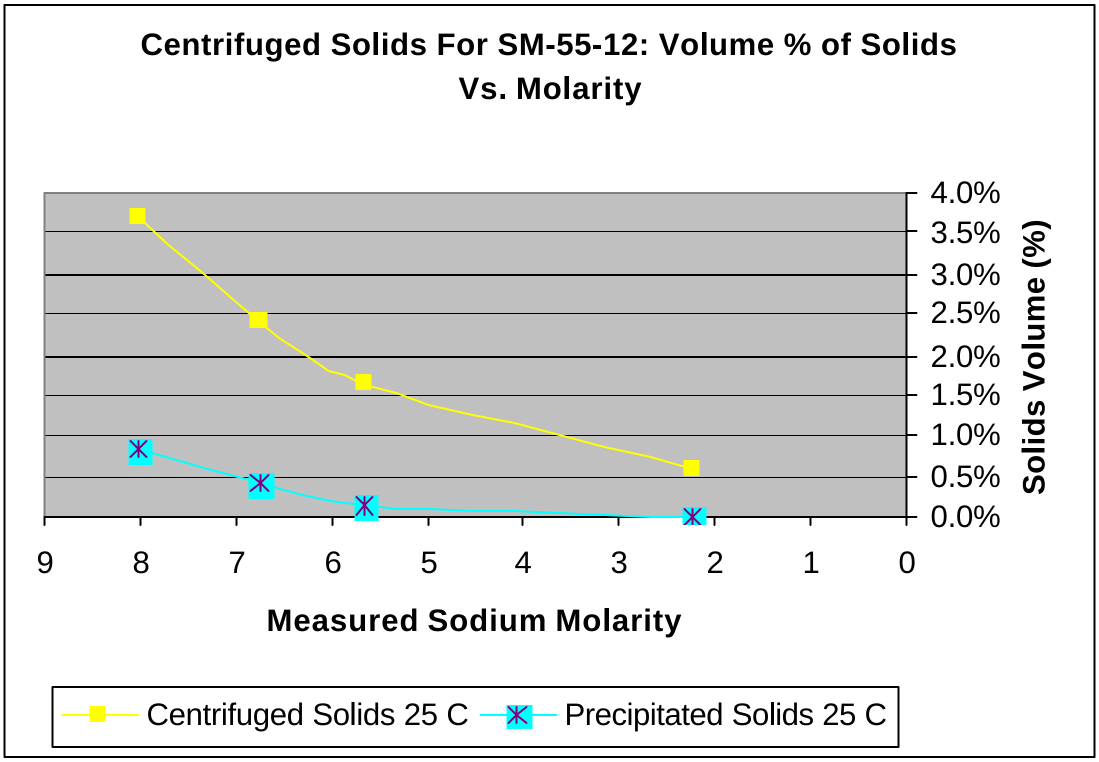

Figure A-50. Solids Volume % of Envelope A Mixture SM-55-12

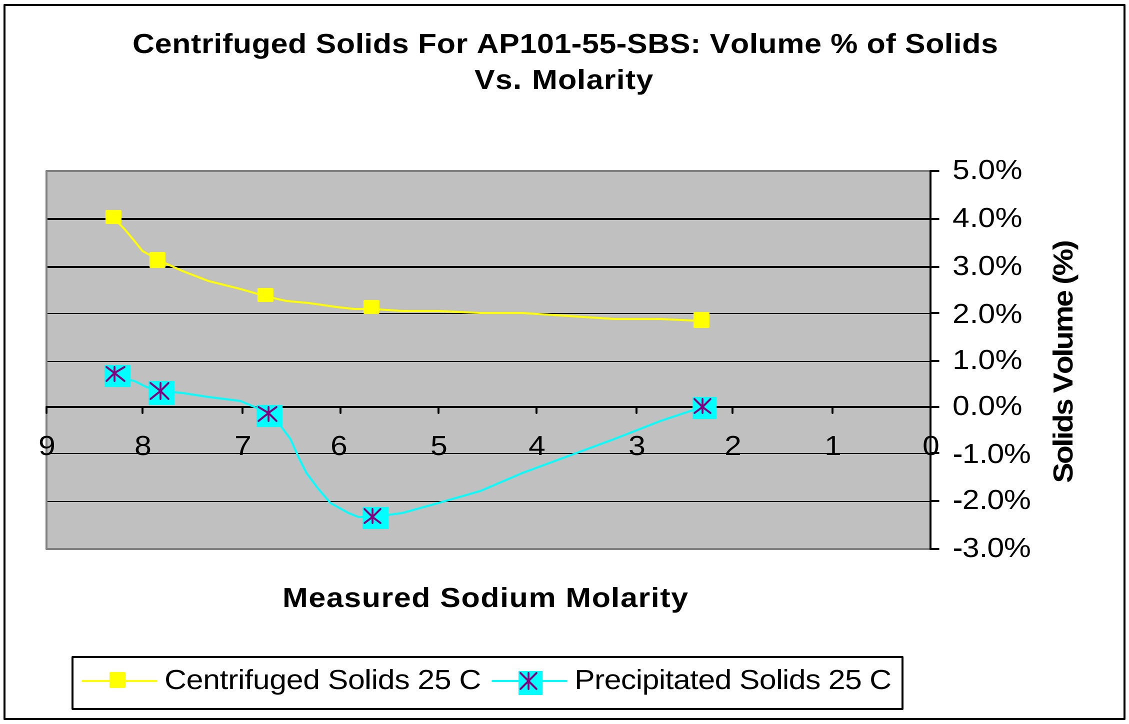

Figure A-51. Solids Volume % of Envelope A Mixture AP101-55%

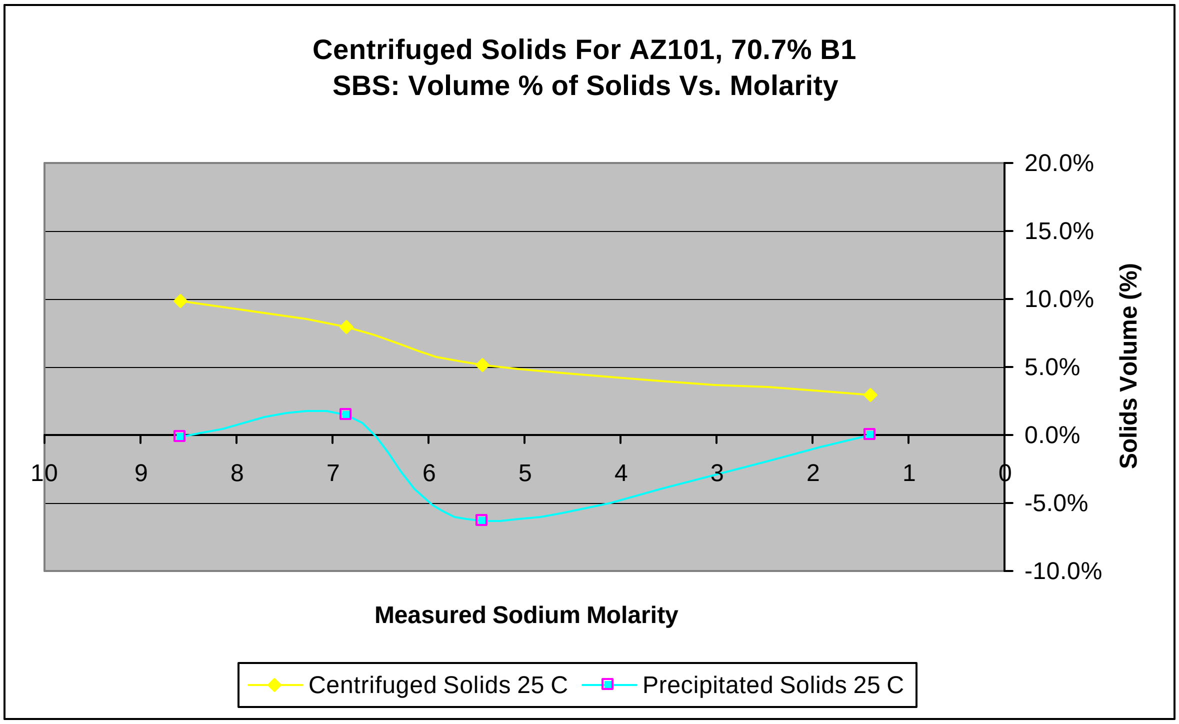

Figure A-52. Solids Volume % of Envelope B Mixture AZ101-70.7% SBS

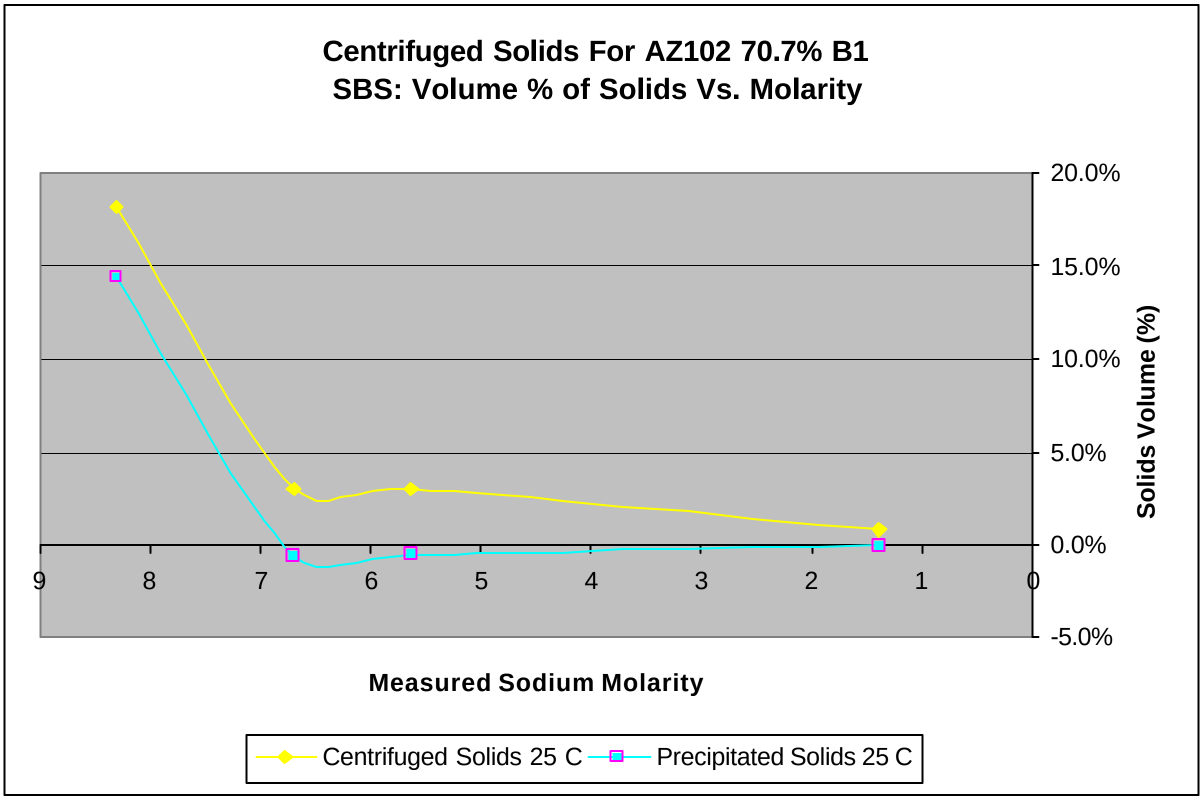

Figure A-53. Solids Volume % of Envelope B Mixture AZ102-70.7% SBS

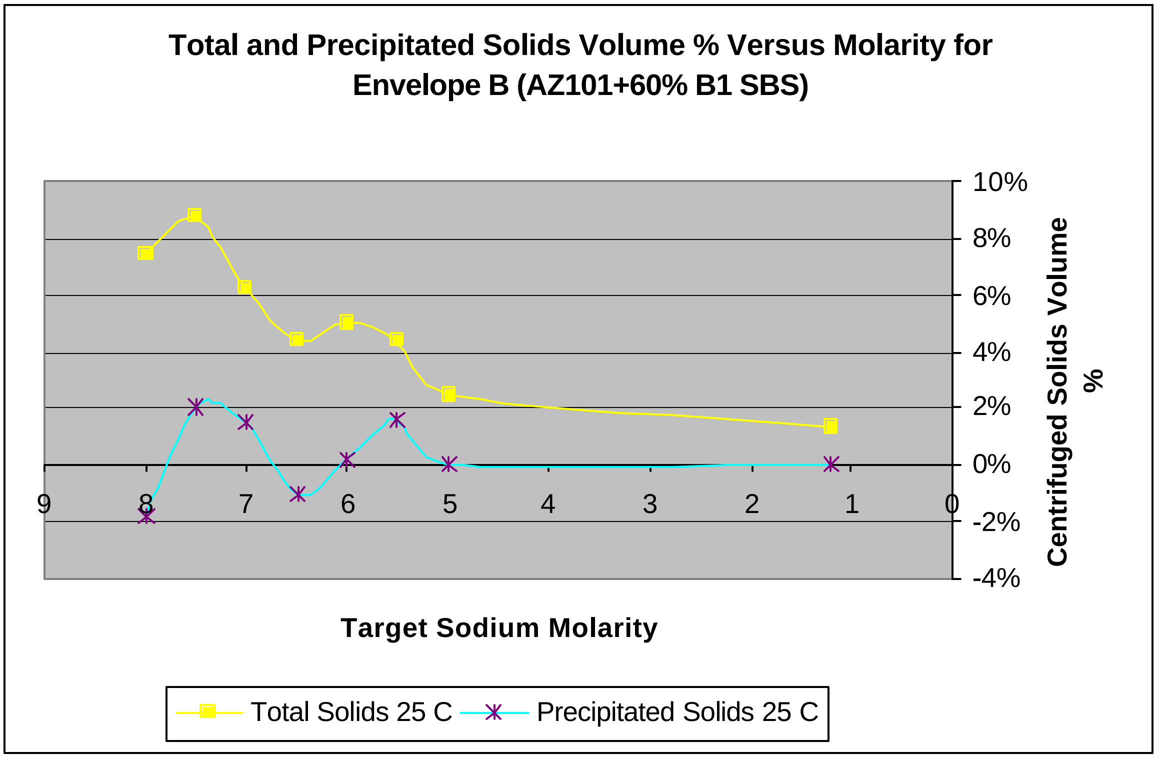

Figure A-54. Solids Volume % of Envelope B Mixture AZ101-60 % SBS

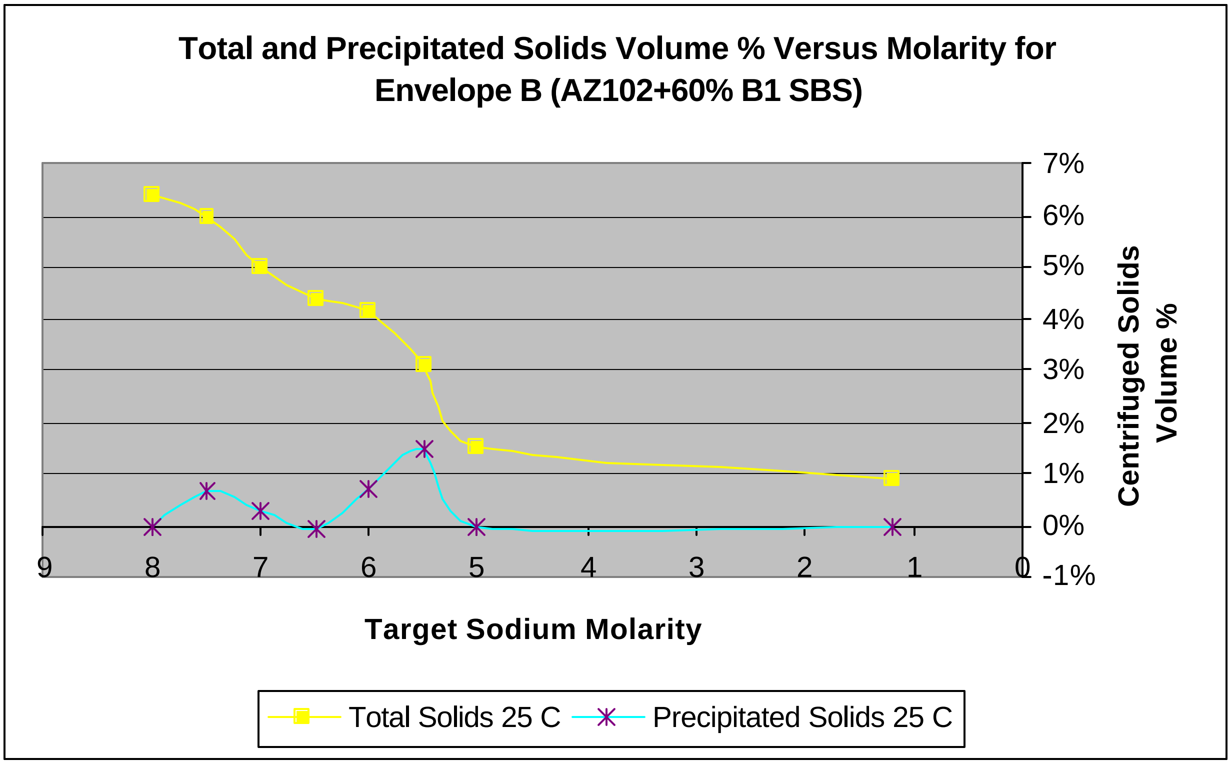

Figure A-55. Solids Volume % of Envelope B Mixture AZ102-60% SBS

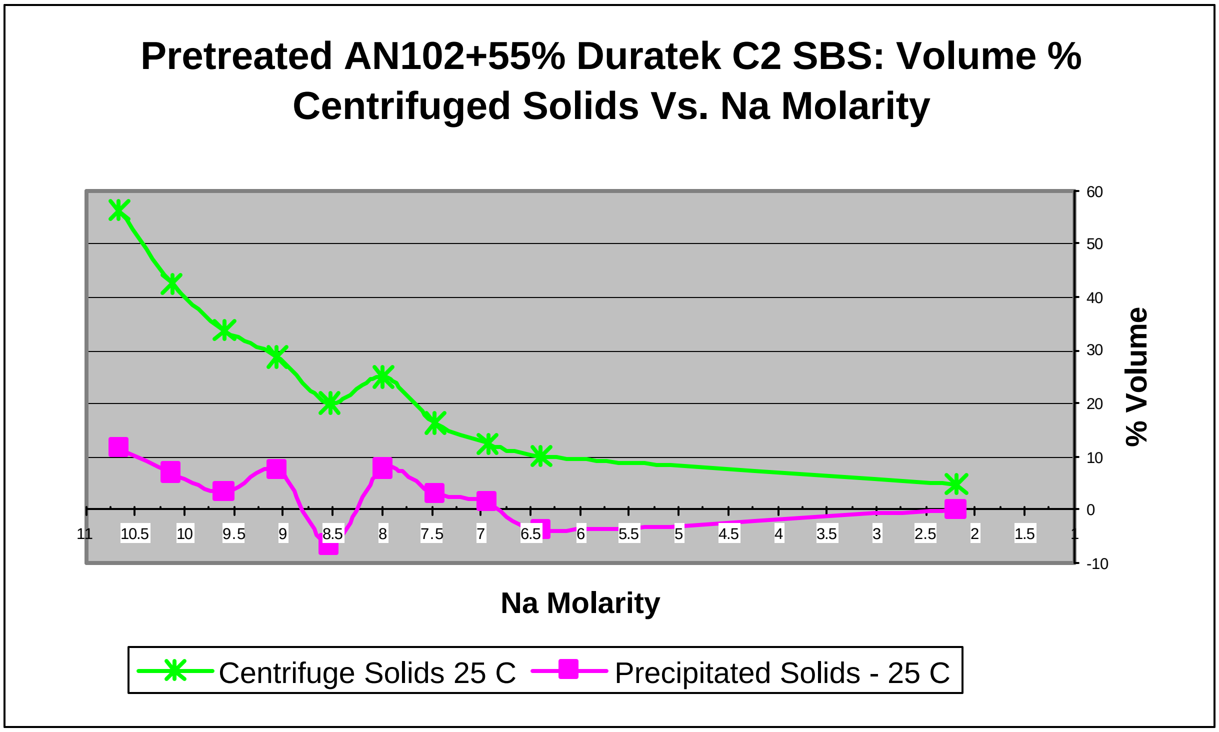

Figure A-56. Solids Volume % of Envelope C Mixture AN102-55% SBS

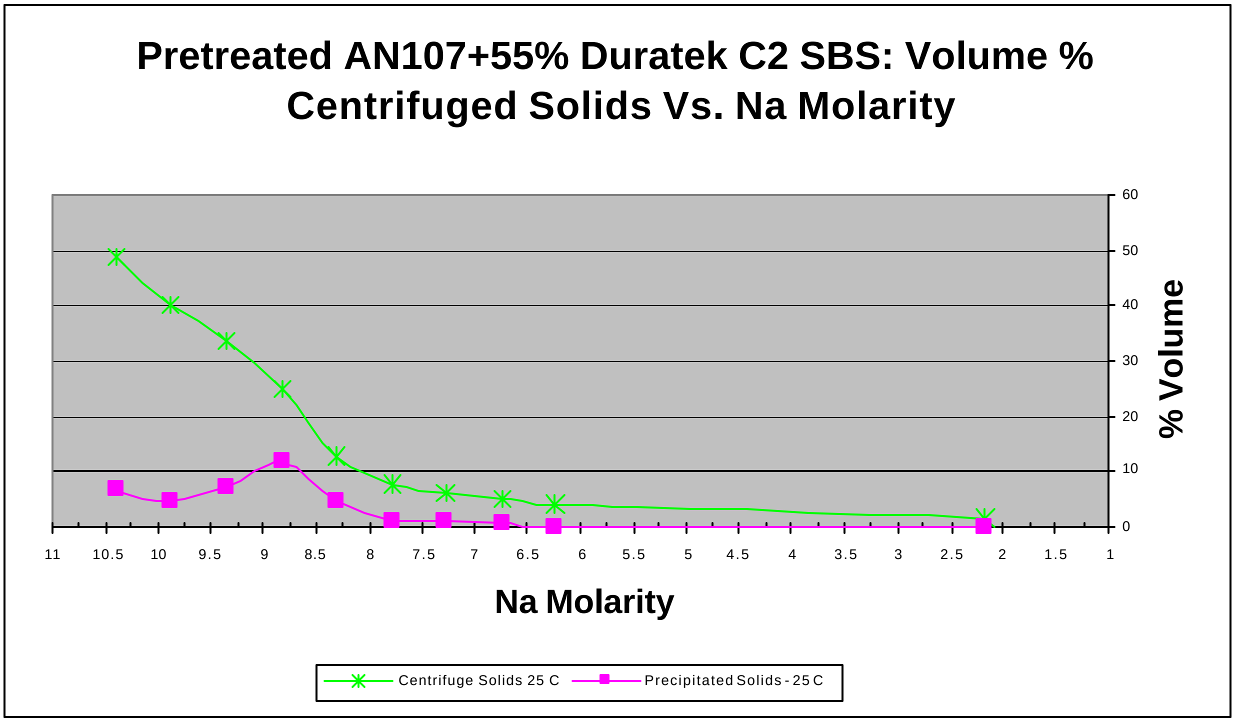

Figure A-57. Solids Volume % of Envelope C Mixture AN107-55% SBS

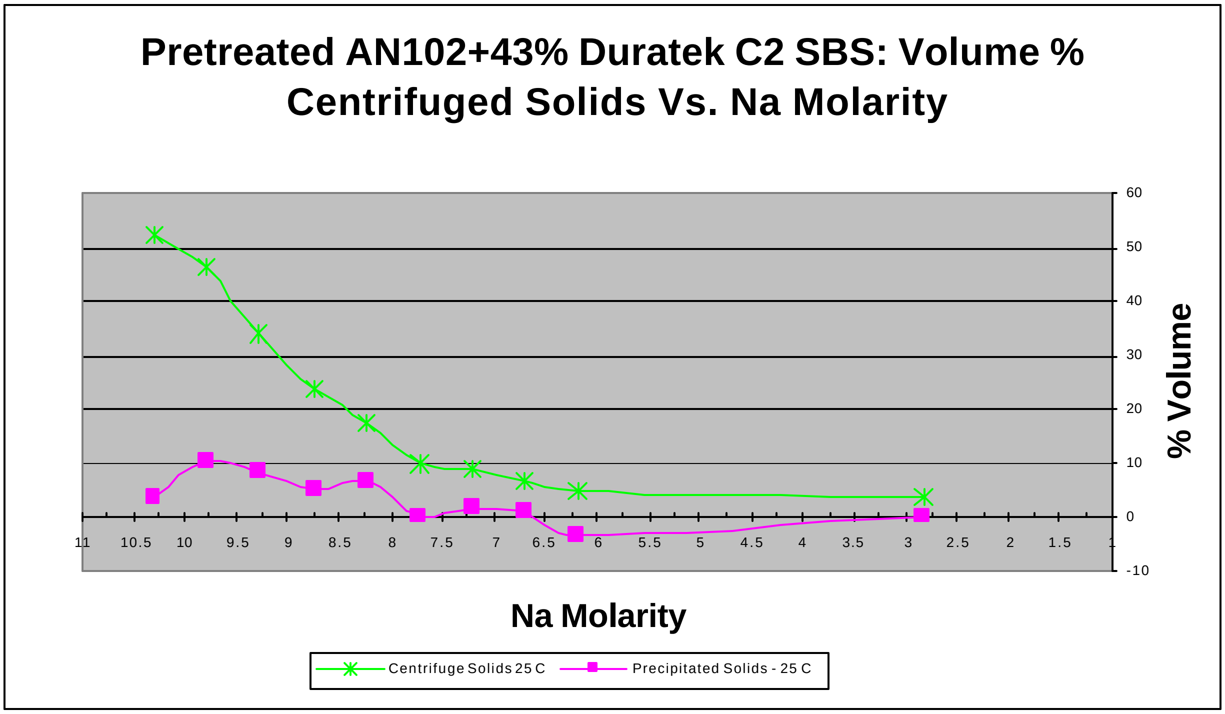

Figure A-58. Solids Volume % of Envelope C Mixture AN102-43% SBS

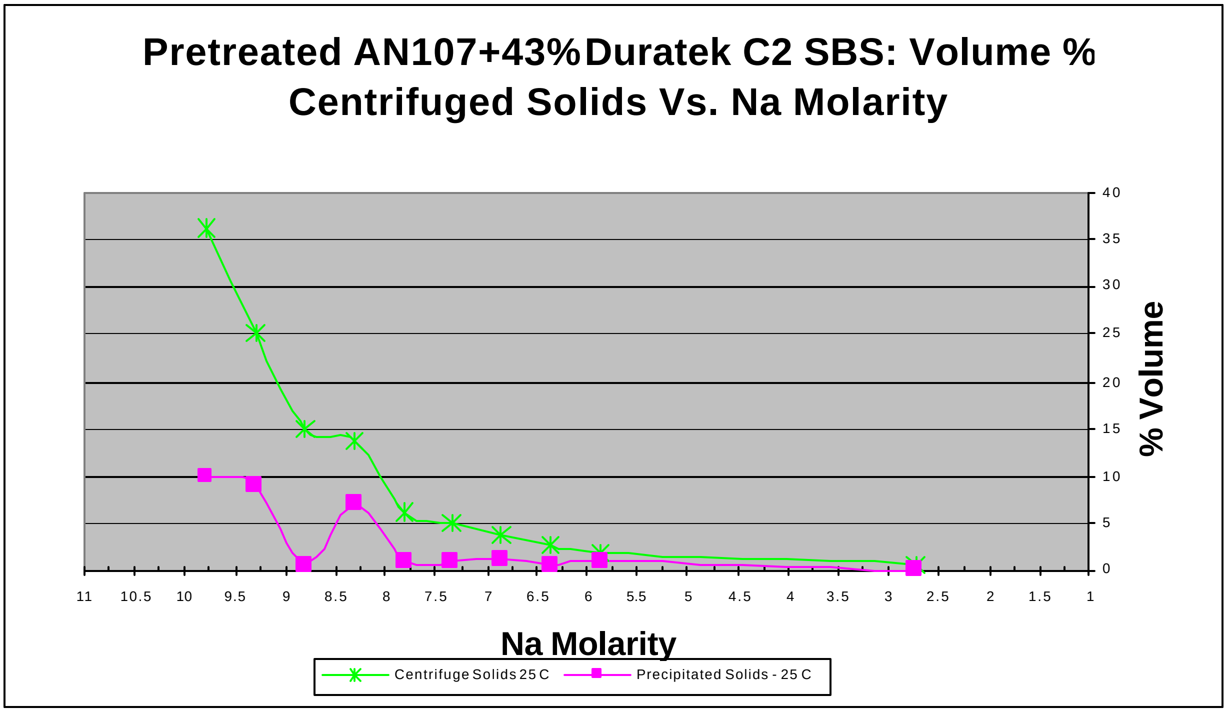

Figure A-59. Solids Volume % of Envelope C Mixture AN107-43% SBS

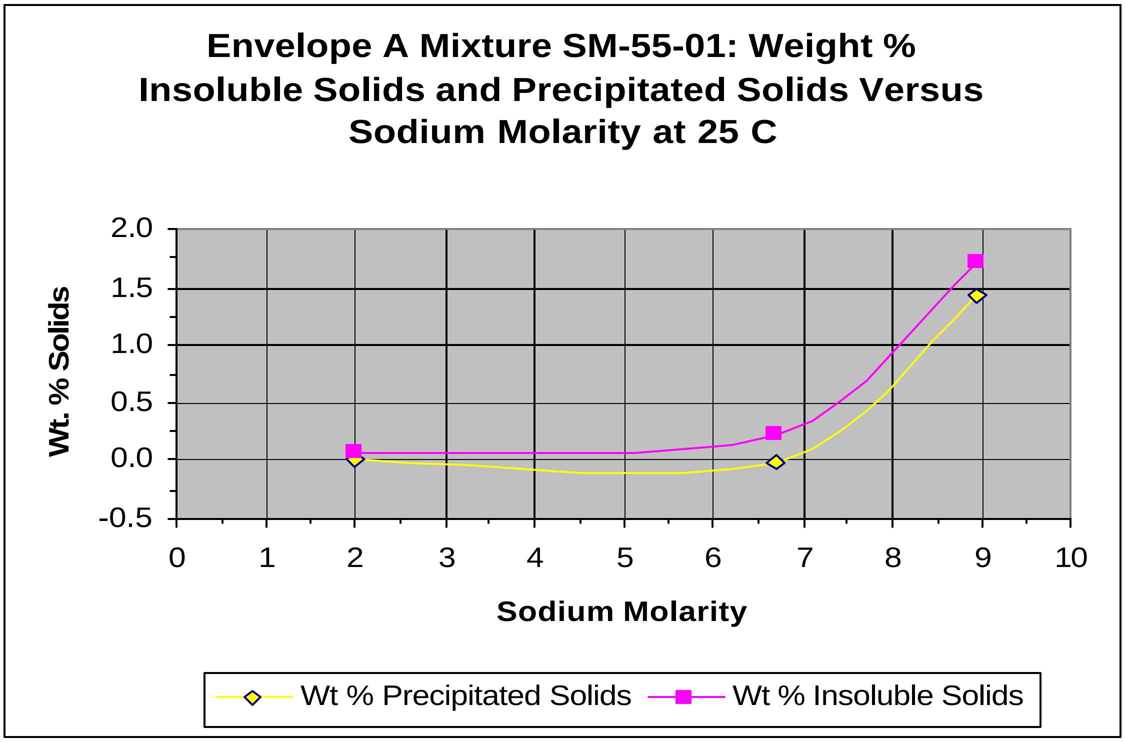

Figure A-60. Wt. % Insoluble and Precipitated Solids for Envelope A Mixture SM-55-01

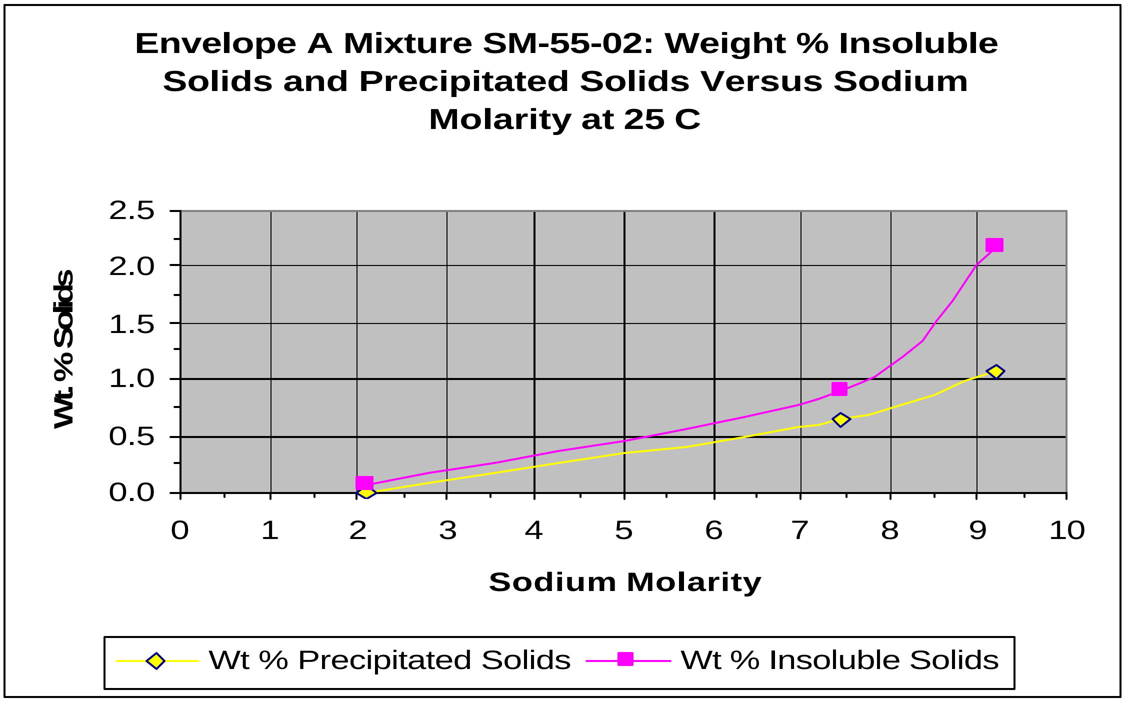

Figure A-61. Wt. % Insoluble and Precipitated Solids for Envelope A Mixture SM-55-02

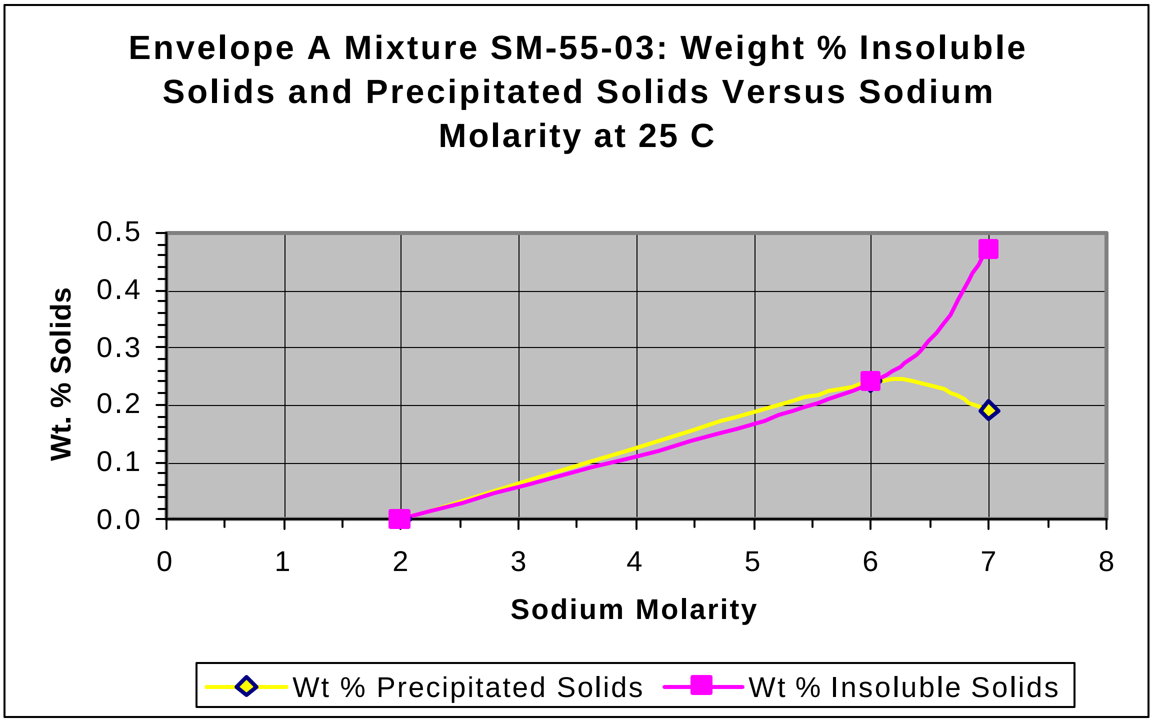

Figure A-62. Wt. % Insoluble and Precipitated Solids for Envelope A Mixture SM-55-03

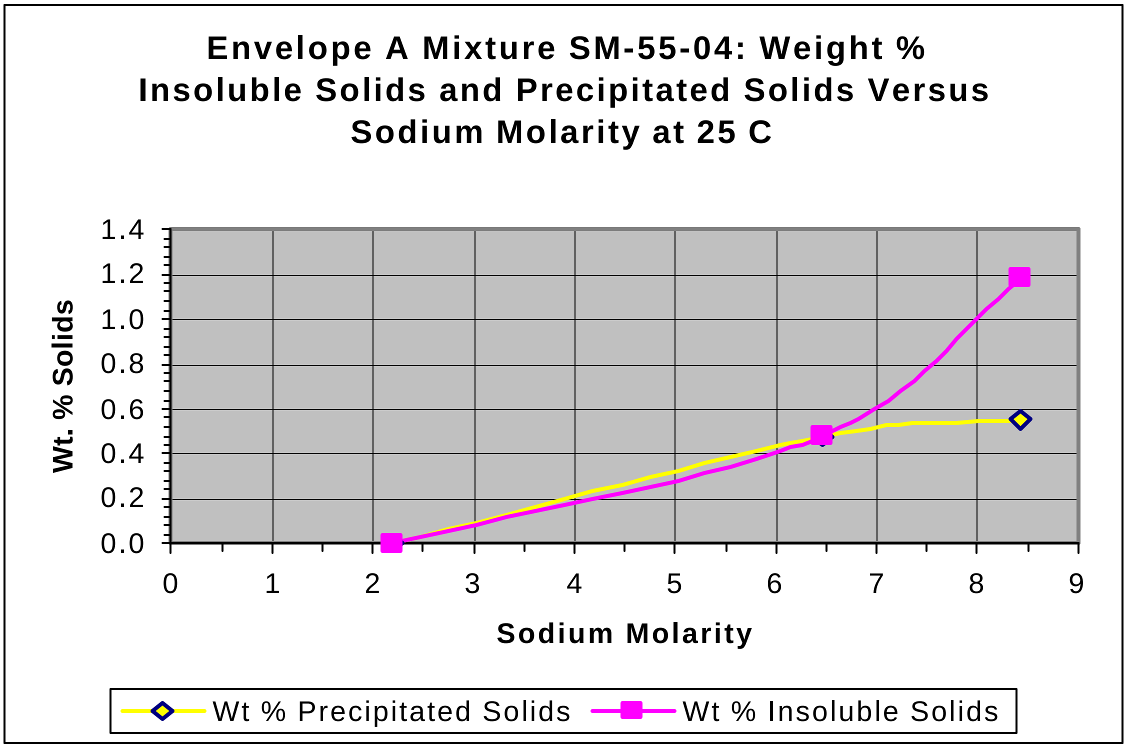

Figure A-63. Wt. % Insoluble and Precipitated Solids for Envelope A Mixture SM-55-04

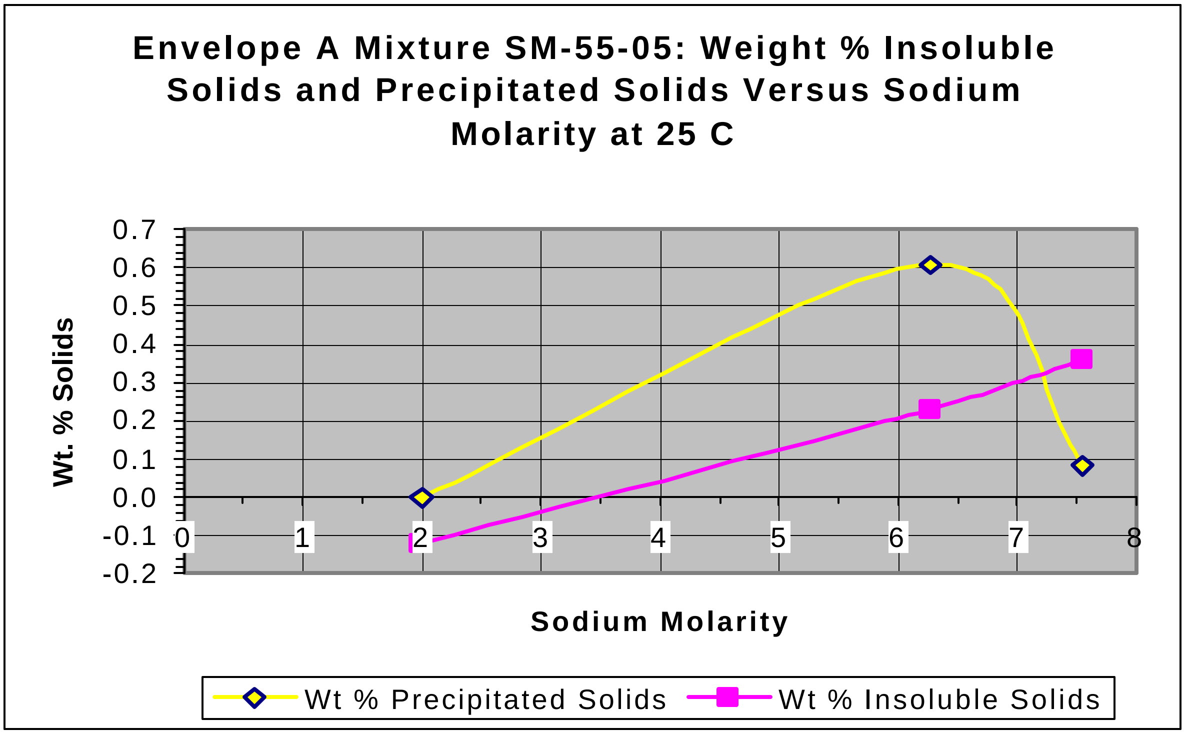

Figure A-64. Wt. % Insoluble and Precipitated Solids for Envelope A Mixture SM-55-05

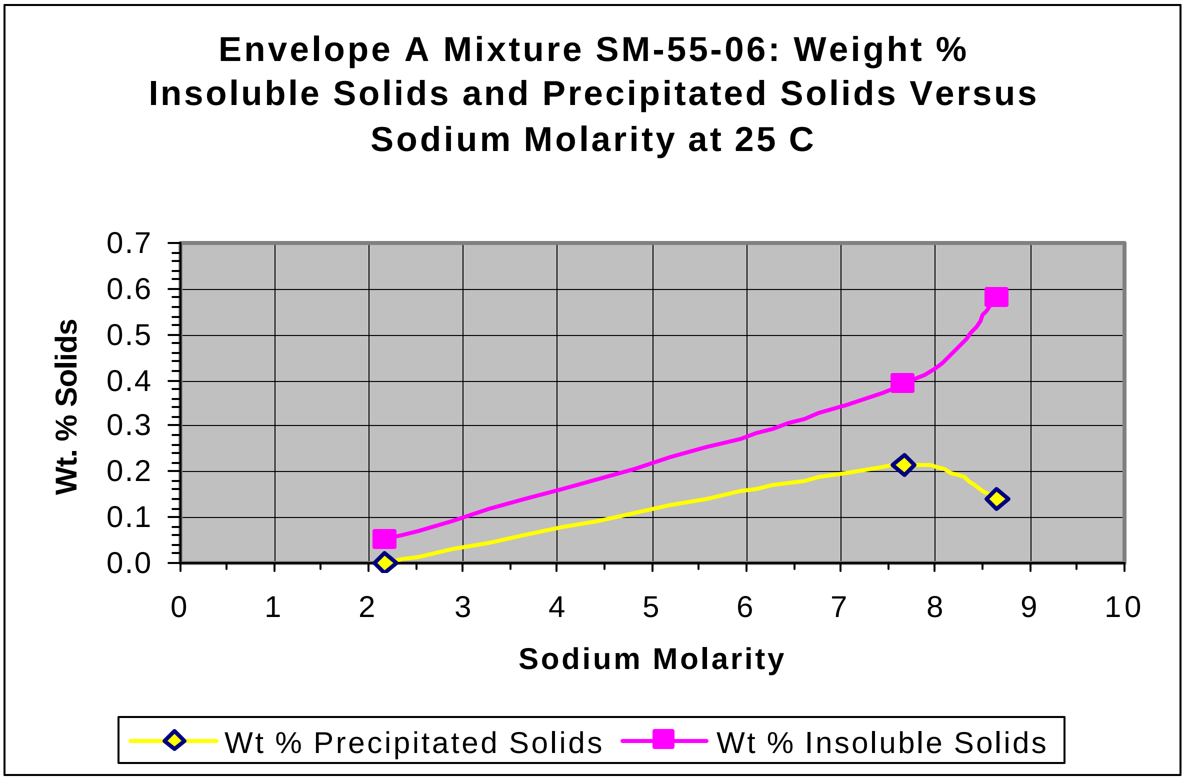

Figure A-65. Wt. % Insoluble and Precipitated Solids for Envelope A Mixture SM-55-06

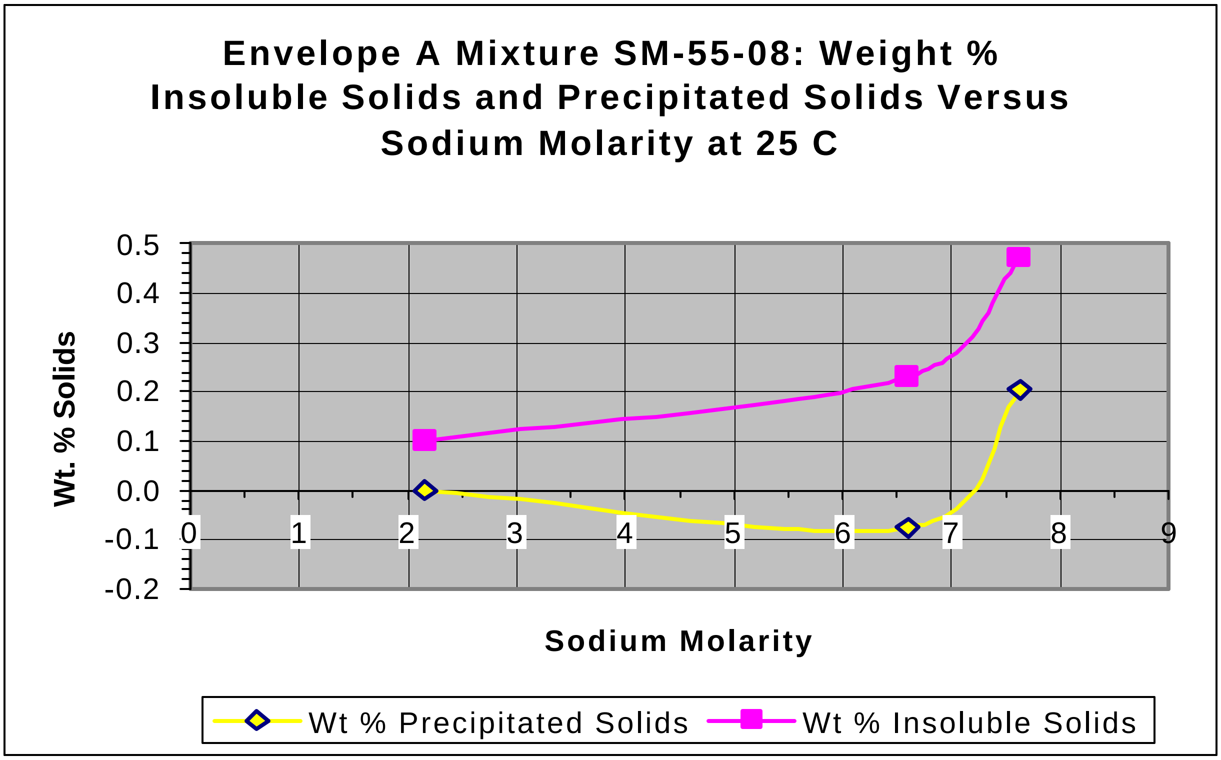

Figure A-66. Wt. % Insoluble and Precipitated Solids for Envelope A Mixture SM-55-08

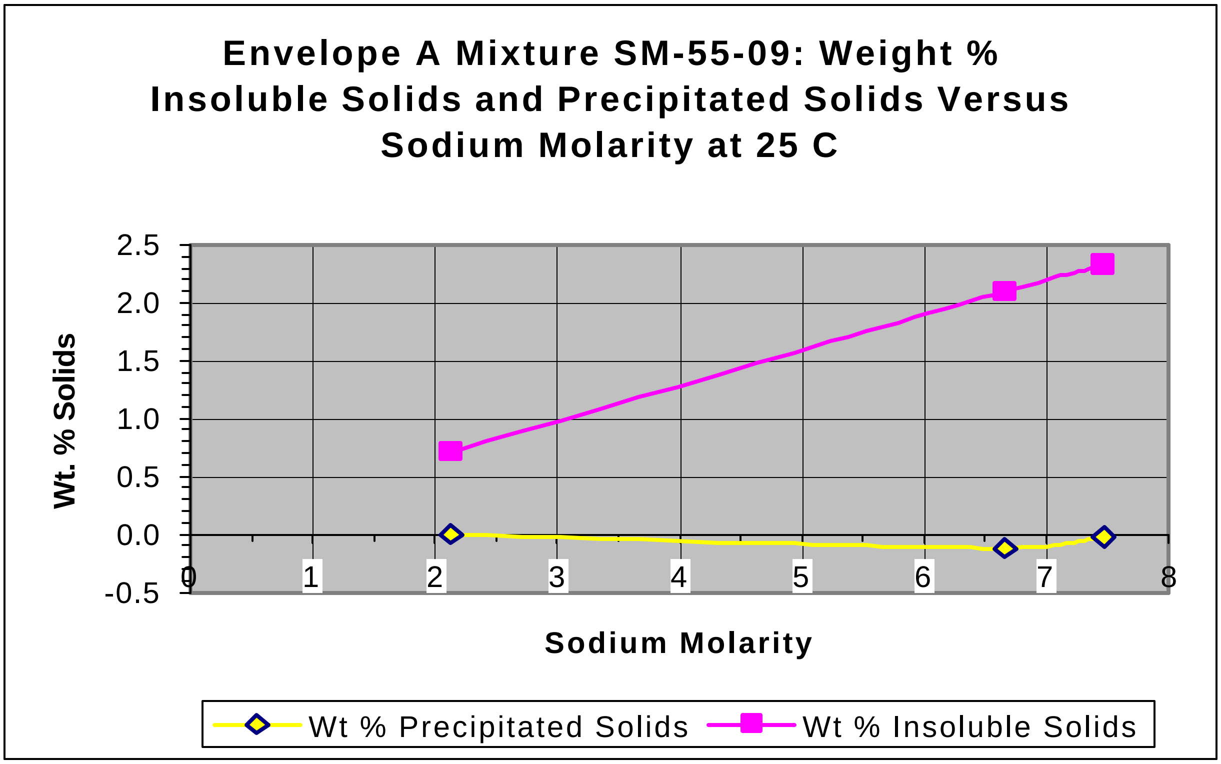

Figure A-67. Wt. % Insoluble and Precipitated Solids for Envelope A Mixture SM-55-09

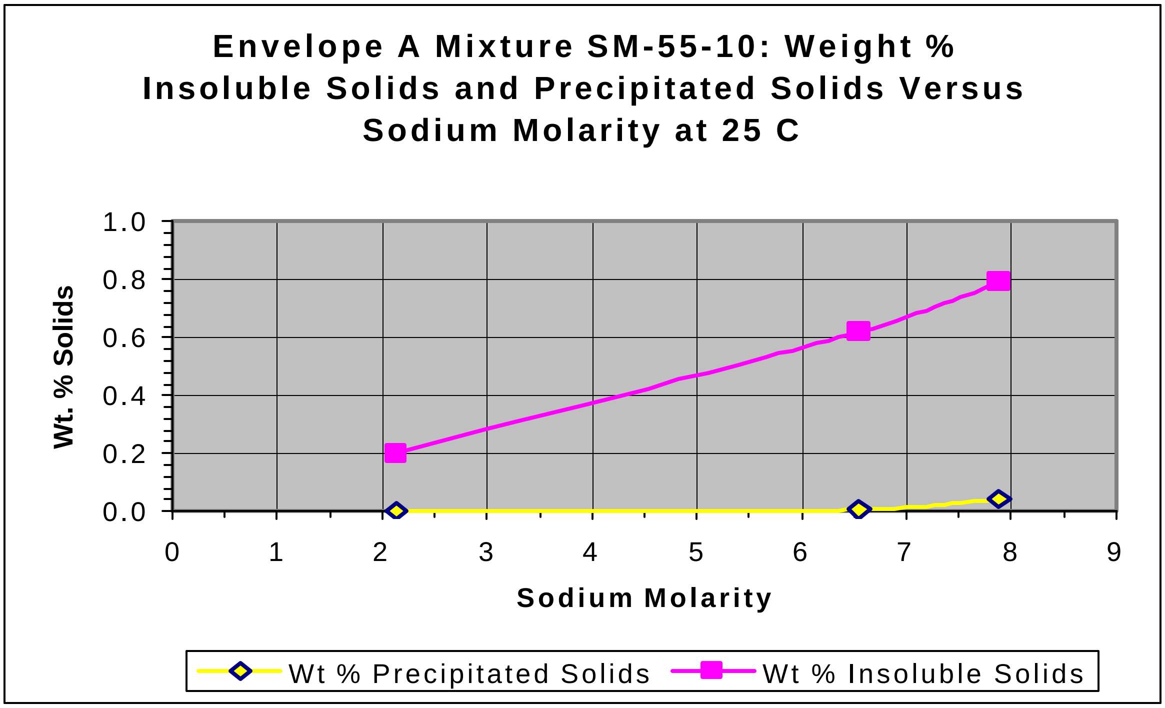

Figure A-68. Wt. % Insoluble and Precipitated Solids for Envelope A Mixture SM-55-10

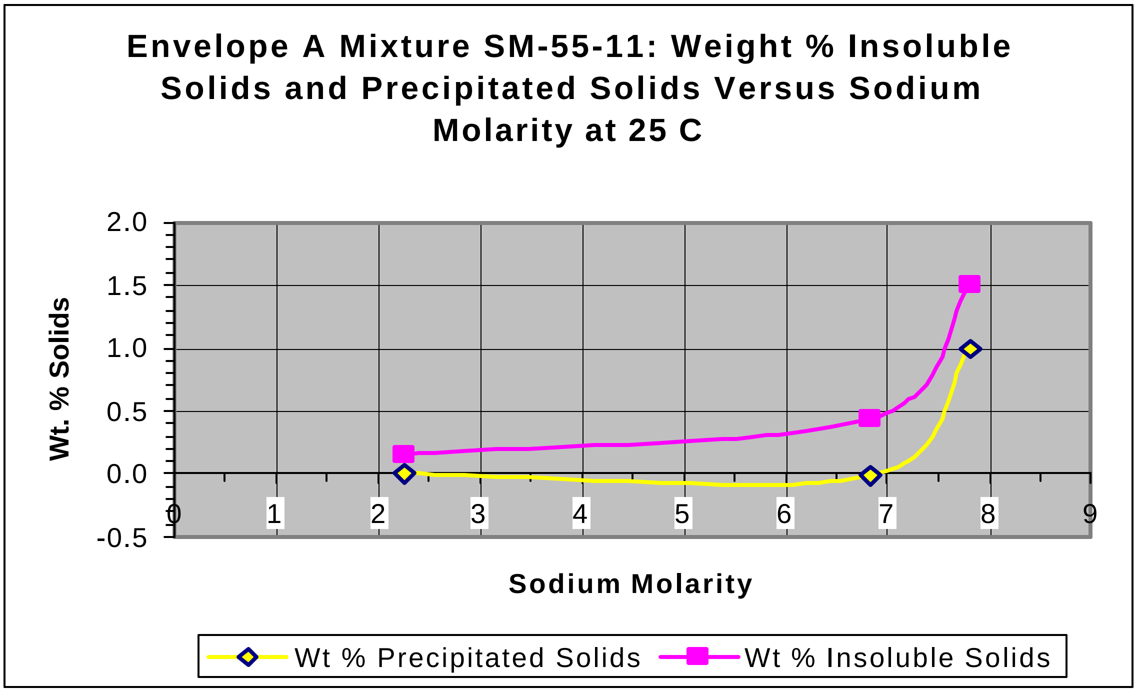

Figure A-69. Wt. % Insoluble and Precipitated Solids for Envelope A Mixture SM-55-11

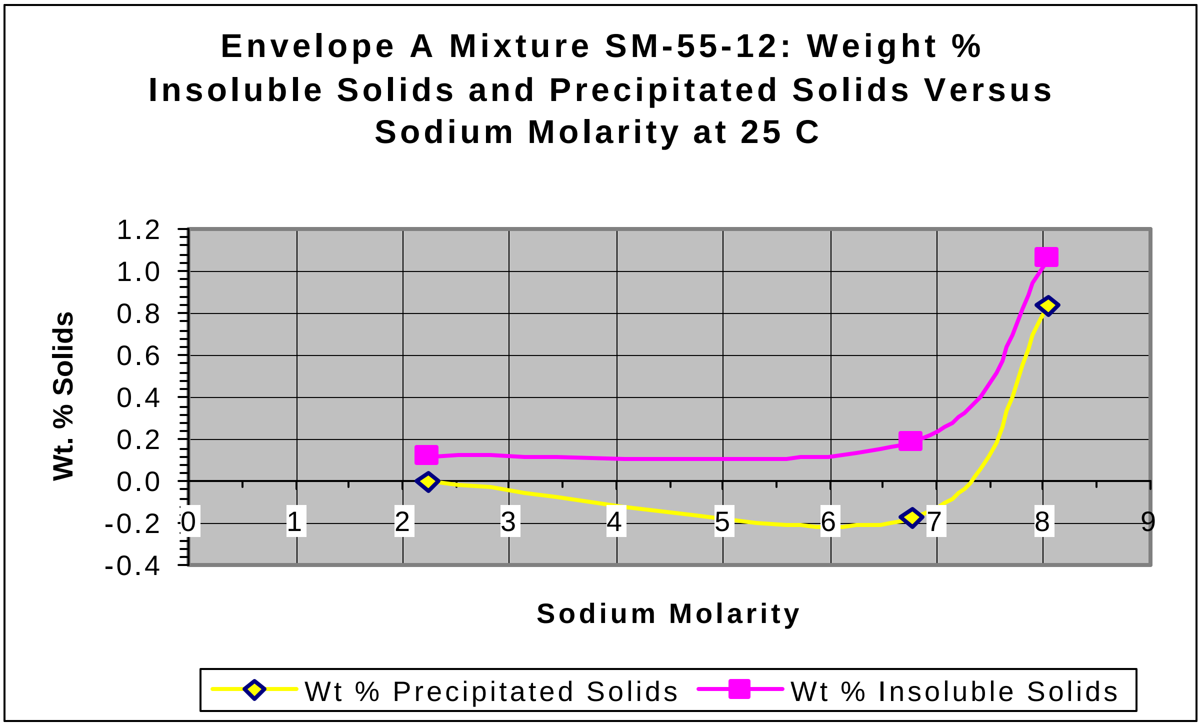

Figure A-70. Wt. % Insoluble and Precipitated Solids for Envelope A Mixture SM-55-12

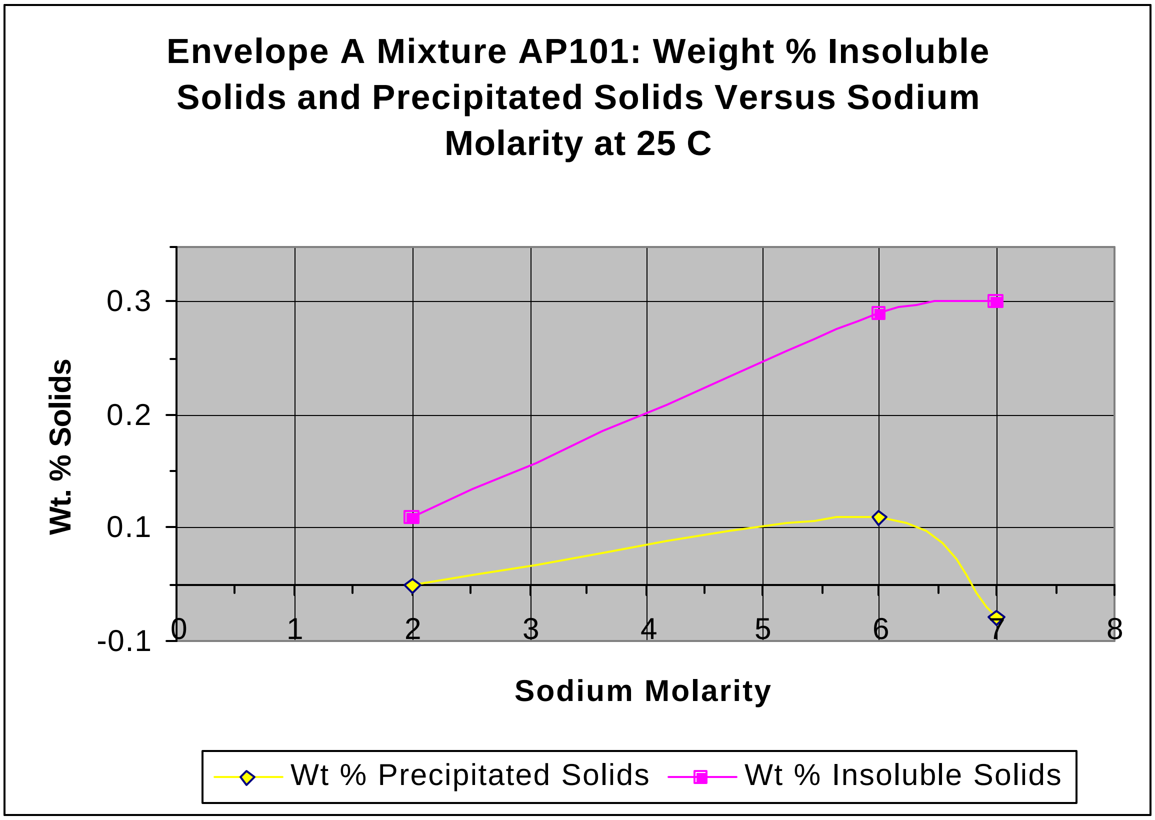

Figure A-71. Wt. % Insoluble and Precipitated Solids for Envelope A Mixture AP101

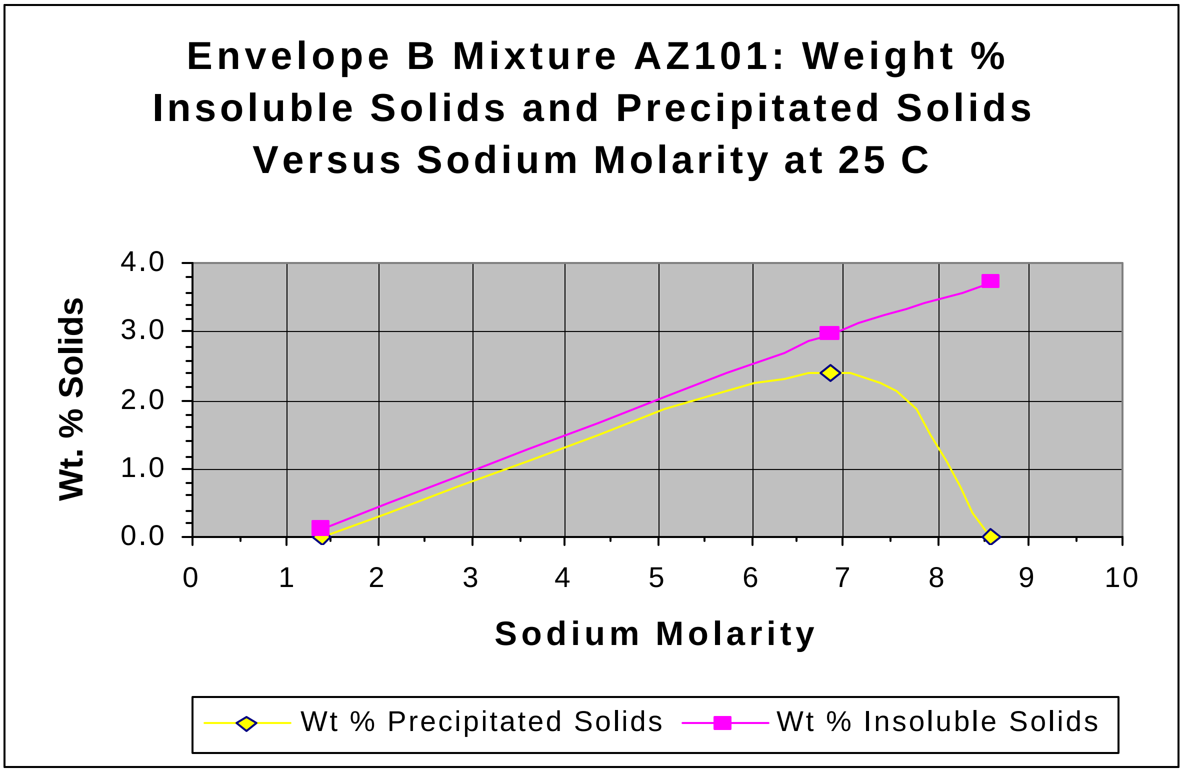

Figure A-72. Wt. % Insoluble and Precipitated Solids for Envelope B Mixture AZ101-70% SBS

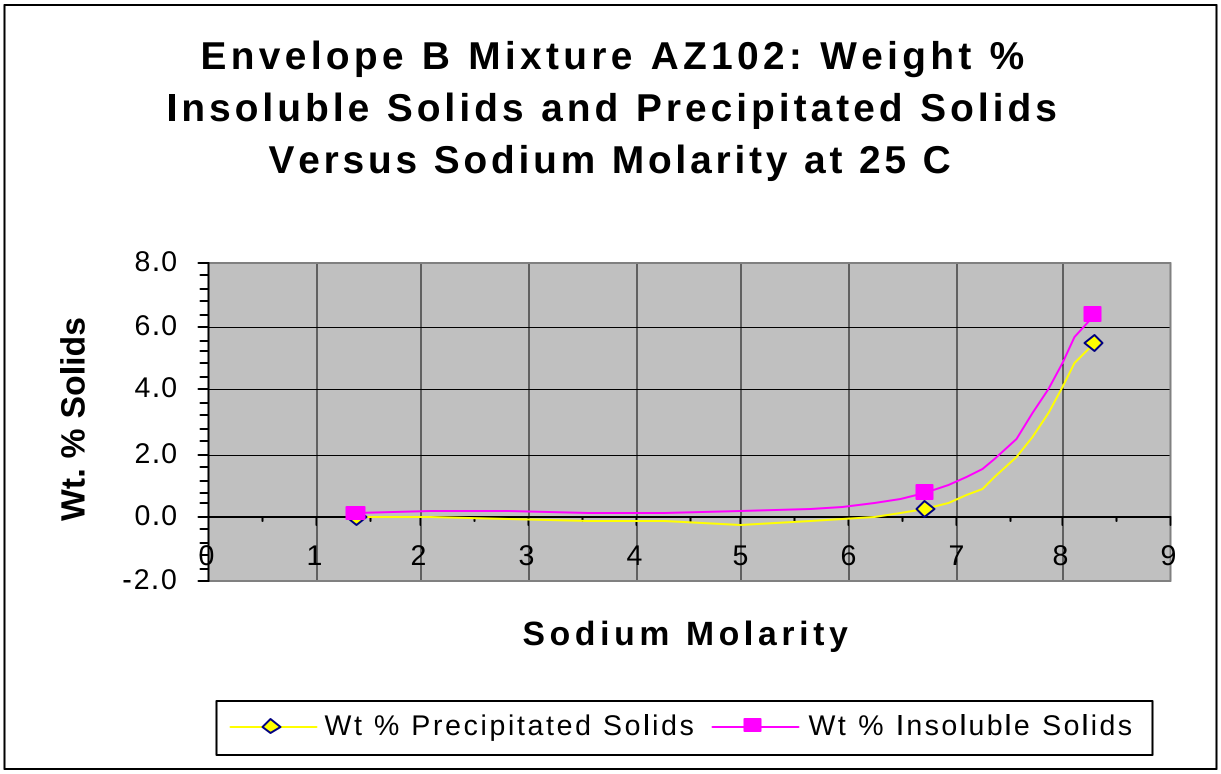

Figure A-73. Wt. % Insoluble and Precipitated Solids for Envelope B Mixture AZ102-70% SBS

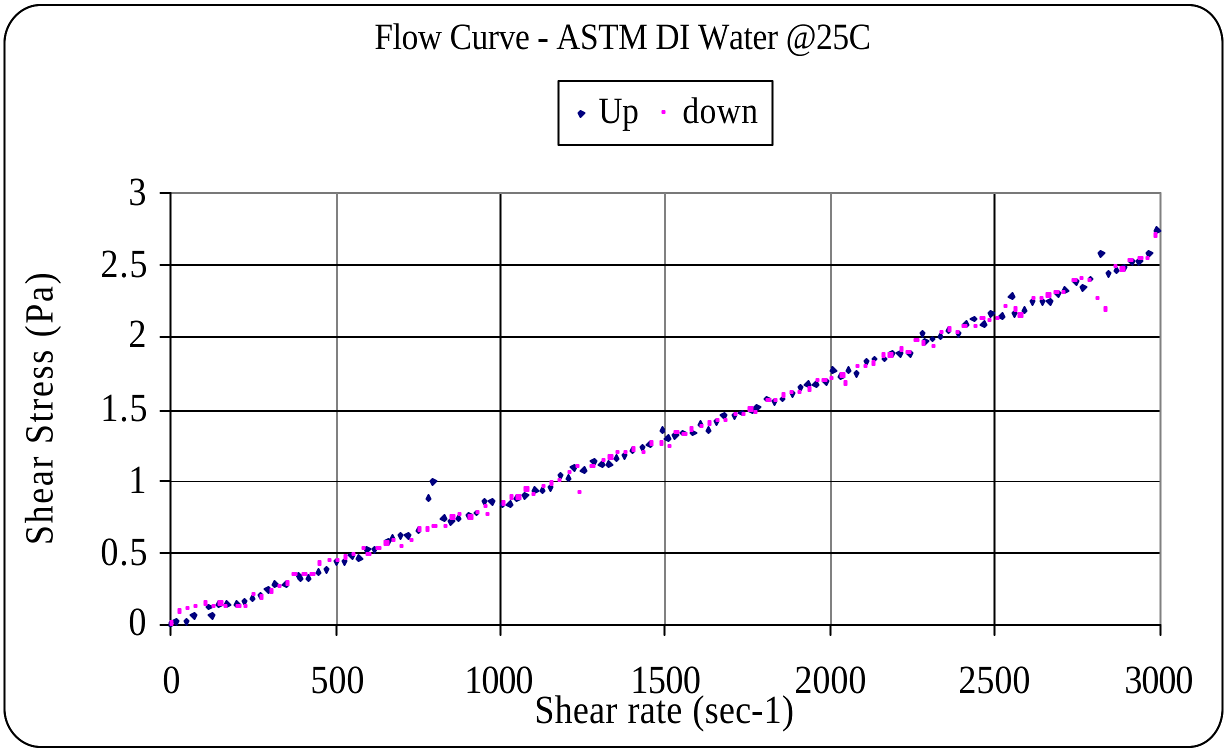

Figure A-74. Single Shear Rate Measurement for 25°C Run

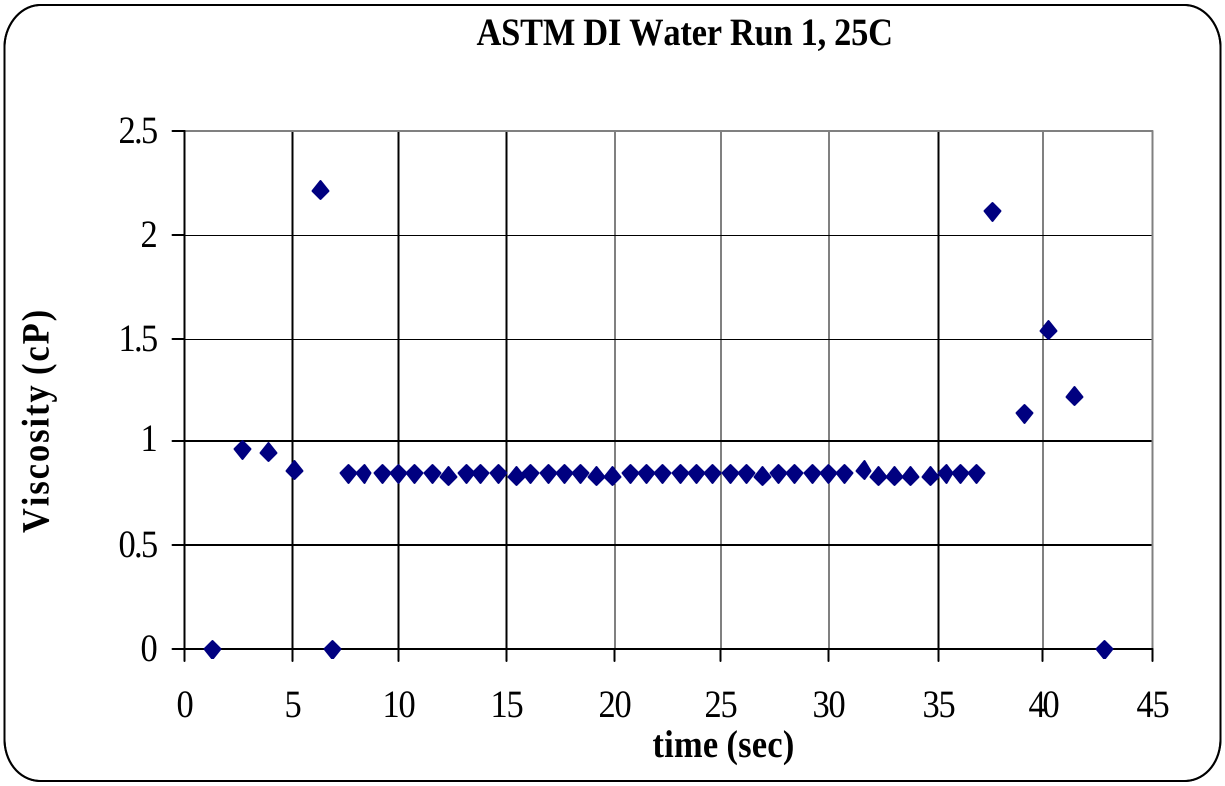

Figure A-75. DI H_2O Flow Curve for 25°C Run

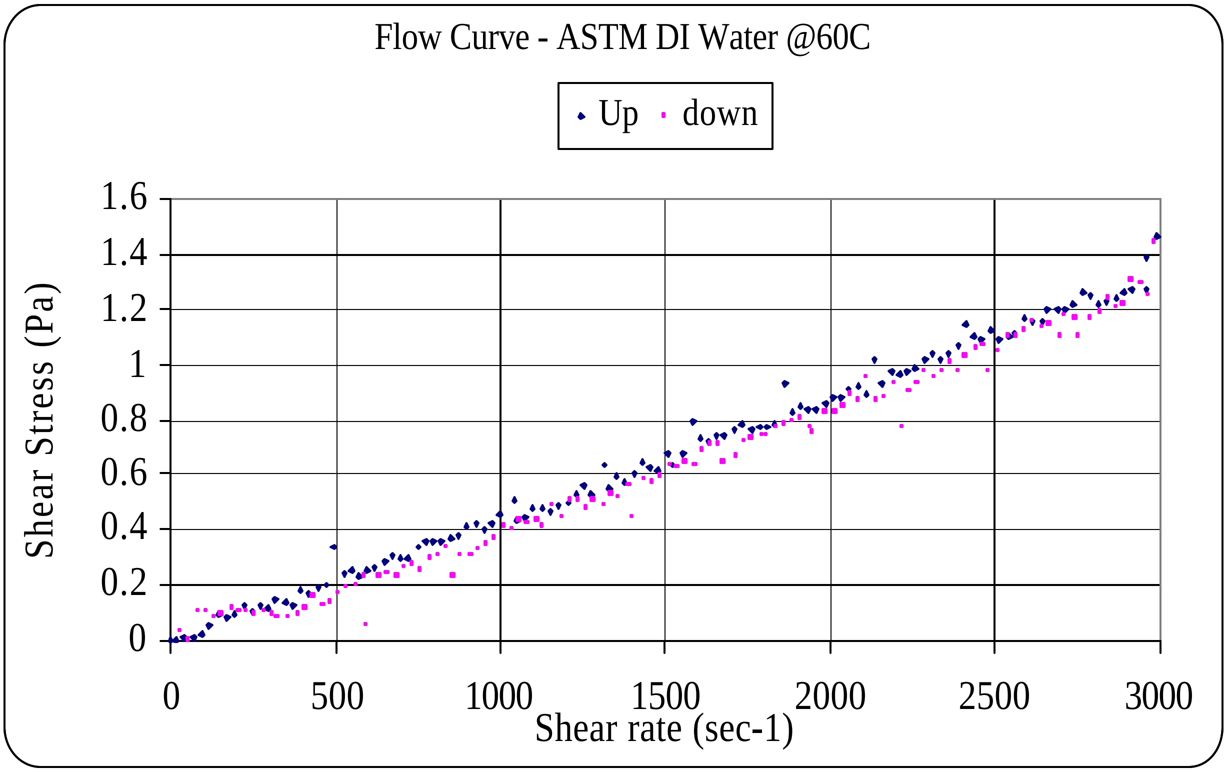

Figure A-76. Single Shear Rate Measurement for 60°C Run

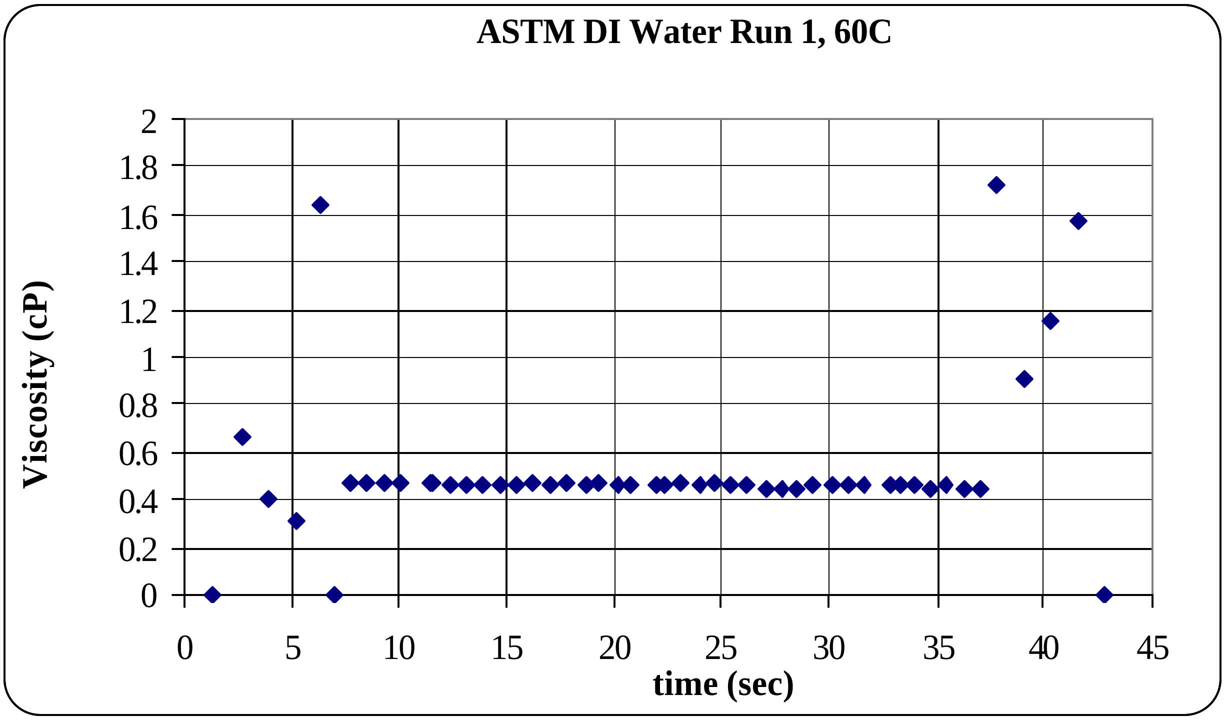

Figure A-77. DI H2O Flow Curve for 60°C Run

Chemical Formula	Chemical Name
(Al2Li(OH)6)2CO3!xH2O	Lithium Aluminum Carbonate Hydroxide Hydrate
NaNO3	Nitratine (Sodium Nitrate)
AlF3H2O	Aluminum Fluoride Hydrate
LiAlF(PO4)	Amblygonite
SiO2	Quartz
Na2CO3!H2O	Thermonatrite
NaAlSiO4	Zeolite A
NaAlSiPO4!xH2O	ZK-21
Al(OH)3	Bayerite, Gibbsite (Aluminum Hydroxide)
KCl	Sylvite (Potassium Chloride)
NaNO2	Sodium Nitrite
Na7F(PO4)2(H2O)19	Natrophosphate
Na3FSO4	Kogarkoite (Sodium FluoroSulfate)
NaF	Villiaumite (Sodium Fluoride)
Na8[AlSiO4]6(NO3)2	Sodalite
Na2C2O4	Natroxalate
Na5Al3CSi3O15	Natrodavyne, high form
Na3AlF6	Cryolite
Na2Ca(CO3)2!2H2O	Pirssonite

Figure A-78. Chemical Formulas and Names of XRD Solids Found in Envelope A, B, and C Mixtures

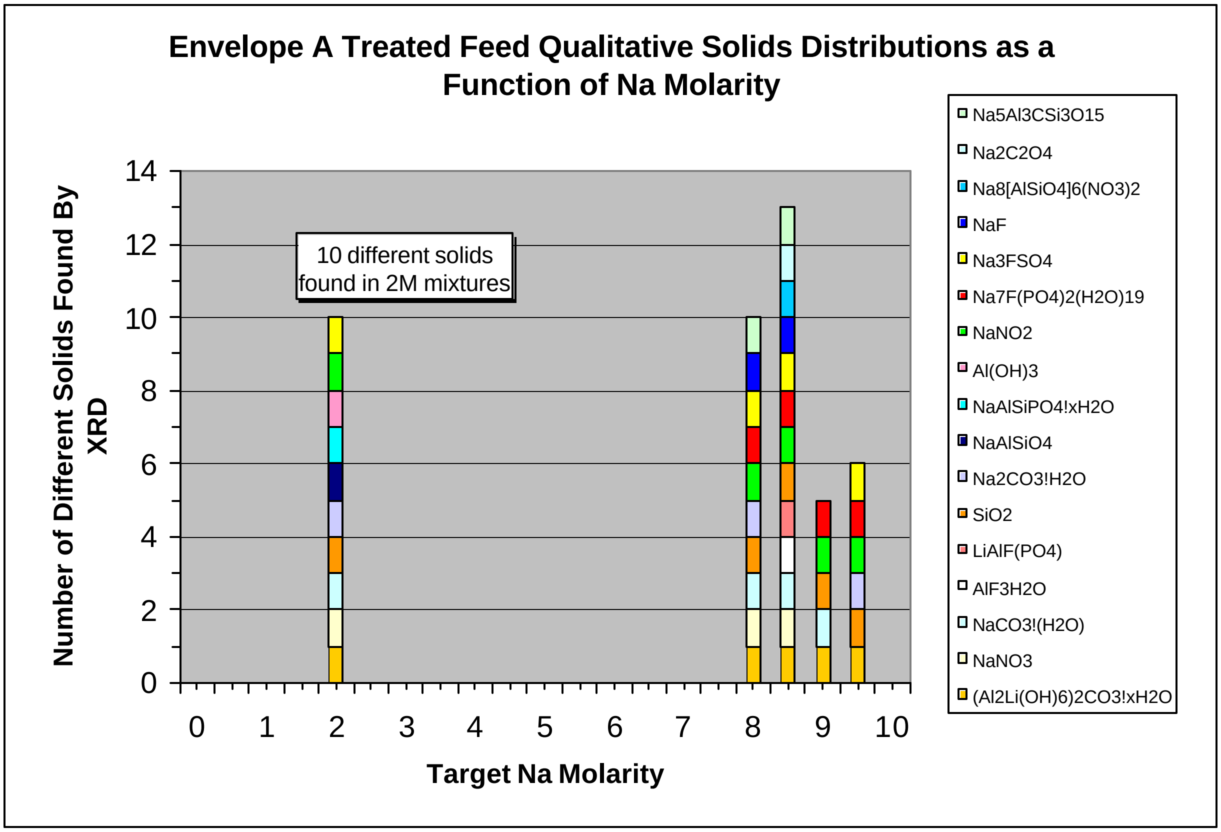

Figure A-79. Envelope A XRD Solids Distribution

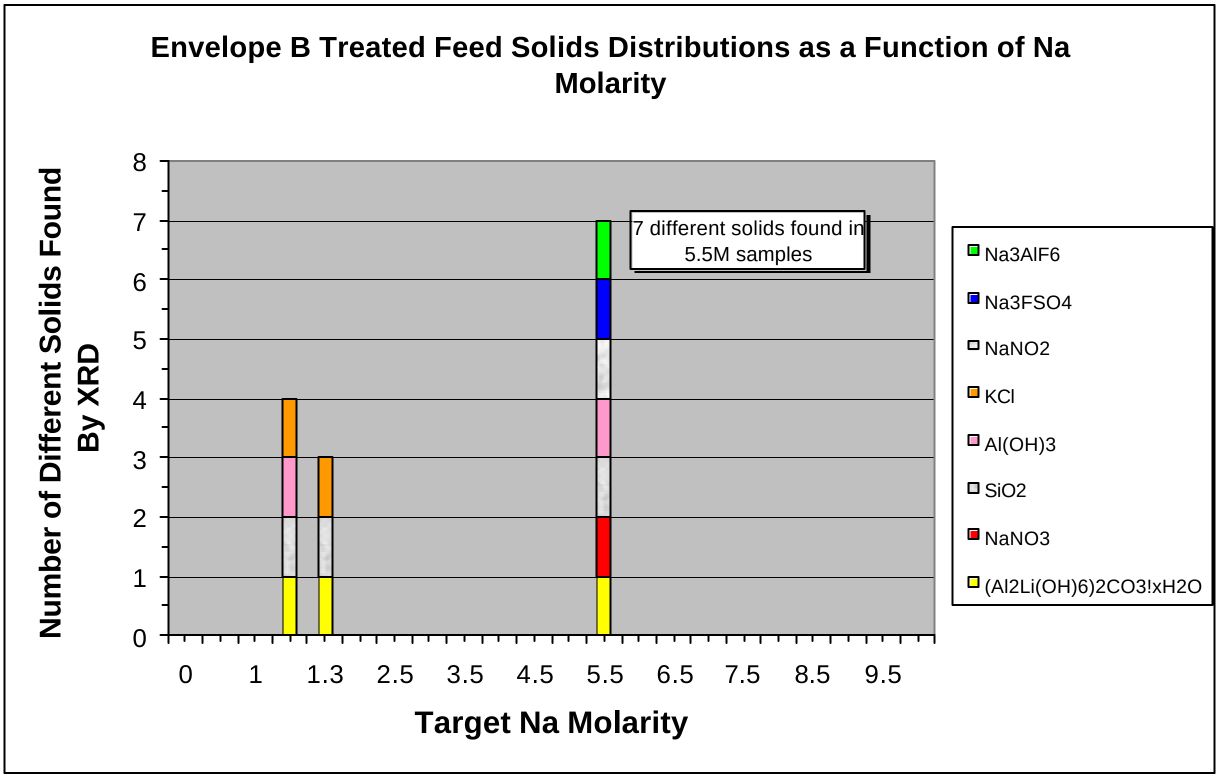

Figure A-80. Envelope B XRD Solids Distribution

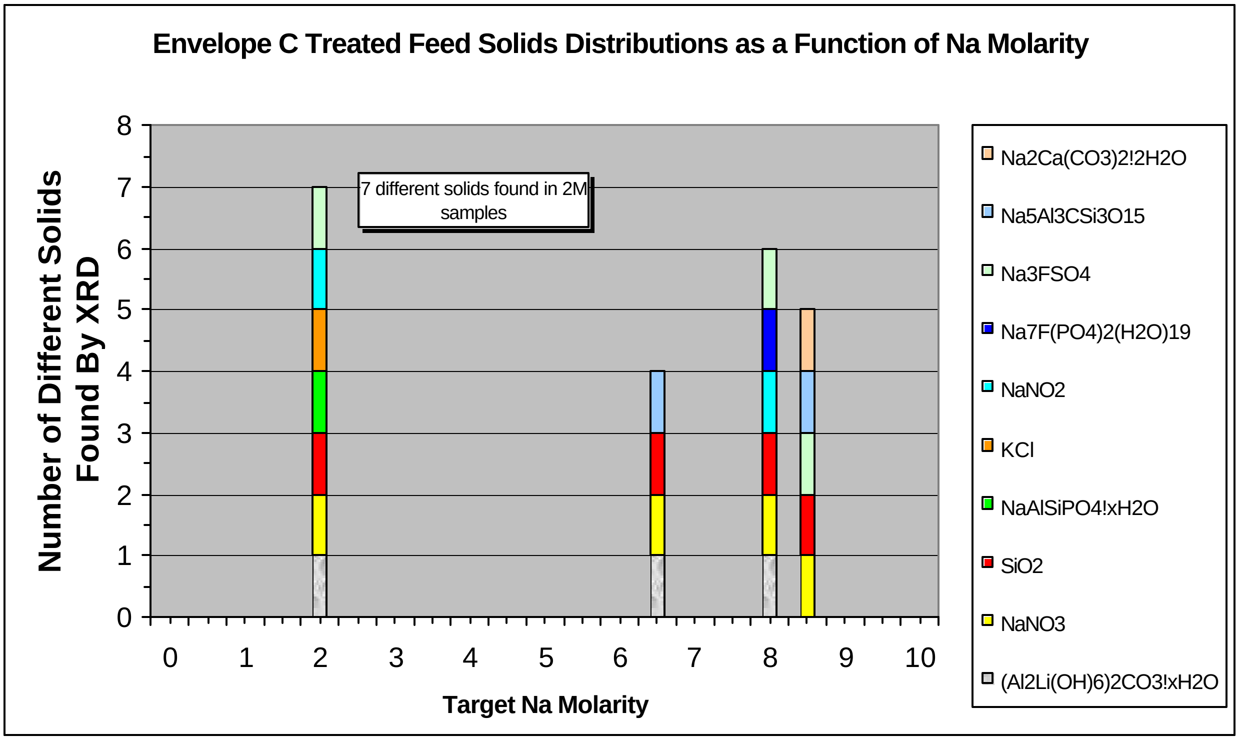

Figure A-81. Envelope C XRD Solids Distribution

(Al2Li(OH)6)2CO3!xH2O	NaNO3	AlF3H2O	LiAlF(PO4)	SiO2	Na2CO3!H2O	NaAlSiO4	NaAlSiPO4!xH2O	Al(OH)3	KCl	NaNO2	Na7F(PO4)2(H2O)19	Na3FSO4	NaF	Na8[AlSiO4]6(NO3)2	Na2C2O4	Na5Al3CSi3O15	Na3AlF6	Na2Ca(CO3)2!2H2O
SM-55-01	SM-55-01			SM-55-01	SM-55-01	SM-55-01		SM-55-01										
SM-55-02	SM-55-02			SM-55-02	SM-55-02					SM-55-02	SM-55-02	SM-55-02						
SM-55-03	SM-55-03			SM-55-03	SM-55-03		SM-55-03			SM-55-03	SM-55-03							
SM-55-04	SM-55-04		SM-55-04	SM-55-04	SM-55-04						SM-55-04	SM-55-04	SM-55-04	SM-55-04				
SM-55-05	SM-55-05	SM-55-05	SM-55-05	SM-55-05	SM-55-05											SM-55-05		
SM-55-06	SM-55-06			SM-55-06	SM-55-06		SM-55-06			SM-55-06	SM-55-06							
SM-55-07	SM-55-07			SM-55-07	SM-55-07			SM-55-07			SM-55-07	SM-55-07						
SM-55-08	SM-55-08			SM-55-08			SM-55-08			SM-55-08	SM-55-08	SM-55-08		SM-55-08	SM-55-08			
SM-55-09	SM-55-09			SM-55-09				SM-55-09				SM-55-09						
SM-55-10	SM-55-10			SM-55-10	SM-55-10			SM-55-10		SM-55-10		SM-55-10	SM-55-10					
SM-55-11	SM-55-11			SM-55-11	SM-55-11						SM-55-11	SM-55-11	SM-55-11			SM-55-11		
SM-55-12				SM-55-12	SM-55-12	SM-55-12		SM-55-12		SM-55-12	SM-55-12	SM-55-12						
AZ101-70-B1	AZ101-70-B1			AZ101-70-B1				AZ101-70-B1				AZ101-70-B1						
AZ102-70-B1				AZ102-70-B1					AZ102-70-B1	AZ102-70-B1		AZ102-70-B1						AZ102-70-B1
AZ101-60-B1	AZ101-60-B1			AZ101-60-B1				AZ101-60-B1	AZ101-60-B1			AZ101-60-B1						
AZ102-60-B1												AZ102-60-B1						
pAN102-55-C2	pAN102-55-C2			pAN102-55-C2	pAN102-55-C2				pAN102-55-C2	pAN102-55-C2	pAN102-55-C2	pAN102-55-C2						
pAN107-55-C2	pAN107-55-C2			pAN107-55-C2	pAN107-55-C2				pAN107-55-C2			pAN107-55-C2				pAN107-55-C2		pAN107-55-C2
pAN102-43-C2	pAN102-43-C2			pAN102-43-C2	pAN102-43-C2		pAN102-43-C2			pAN102-43-C2	pAN102-43-C2	pAN102-43-C2				pAN102-43-C2		
	pAN107-43-C2			pAN107-43-C2	pAN107-43-C2							pAN107-43-C2				pAN107-43-C2		pAN107-43-C2

Figure A-82. Solids Found in Envelope A, B, and C Mixtures

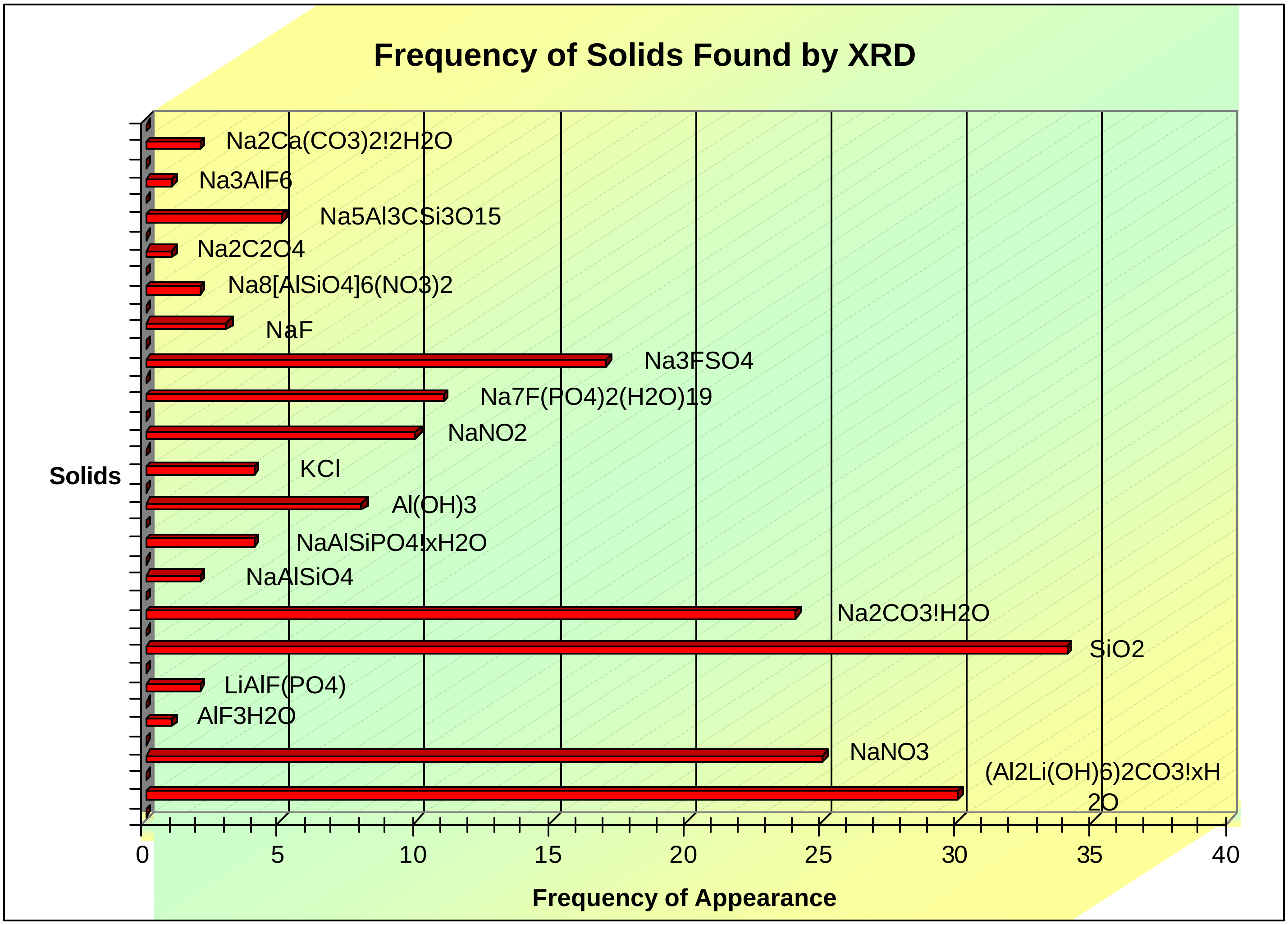

Figure A-83. Total Frequency of Solids in Envelope A, B, and C Mixtures

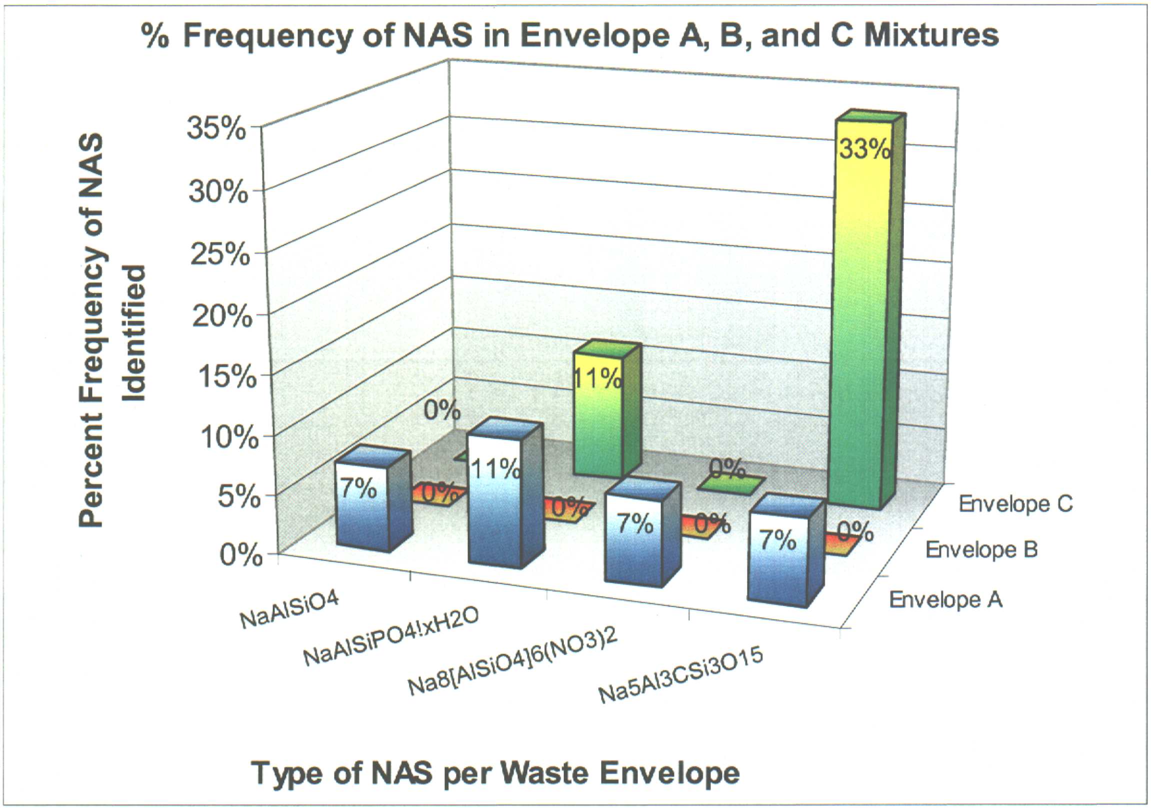

Figure A-84. Individual Types of NAS per Waste Envelope

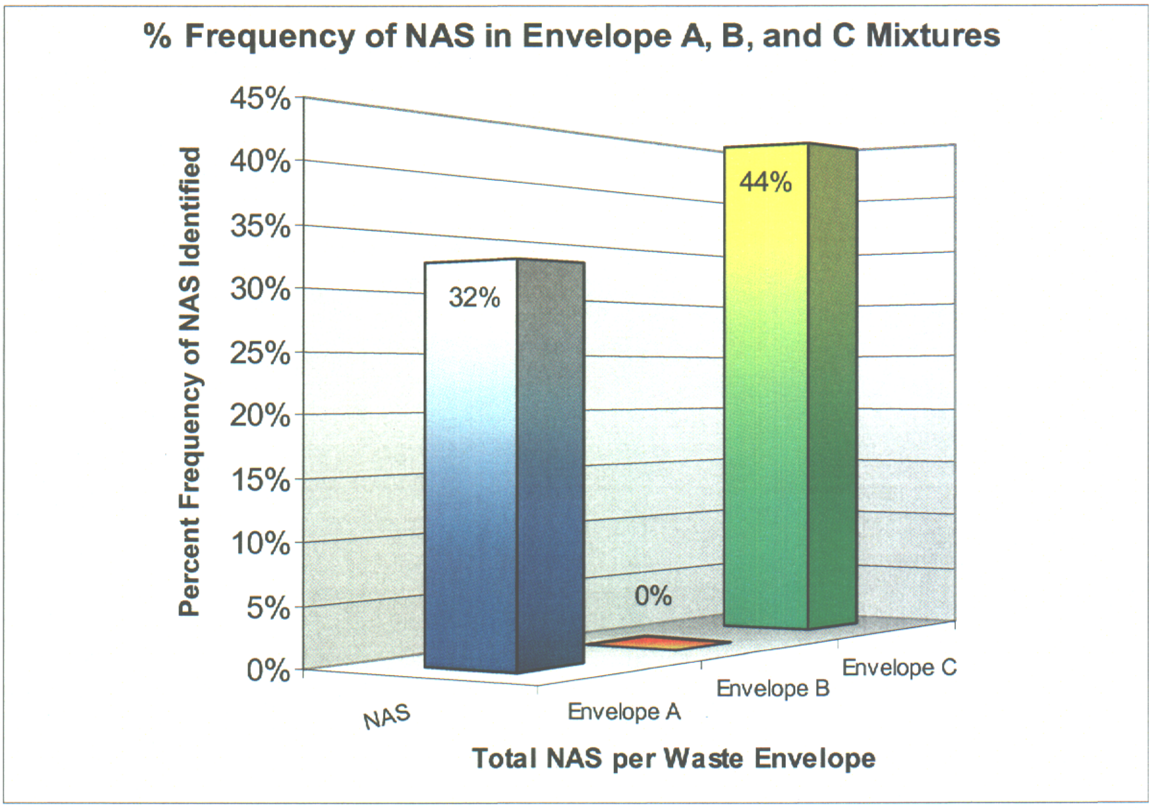

Figure A-85. Total NAS per Waste Envelope