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WSRC-TR-2004-00560 Rev. 0

EVALUATION OF FLUIDIZED BED STEAM REFORMING (FBSR) TECHNOLOGY FOR SODIUM BEARING WASTES FROM IDAHO AND HANFORD USING THE BENCH-TOP STEAM REFORMER (BSR) (U)

FEBRUARY 2005

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Immobilization Technology Section
Savannah River National Laboratory
Aiken, SC 29808

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LIST OF ACRONYMS

ANL-W	Argonne National Laboratory-West
BSR	Bench-top Steam Reformer
COT	Continuous Operating Time
CWF	Ceramic Waste Form
DOE	Department of Energy
GC	Gas Chromatograph
ICP-ES	Inductively Coupled Plasma Emission Spectroscopy
INEEL	Idaho National Engineering and Environmental Laboratory
FBSR	Fluidized Bed Steam Reformer
LAW	Low Activity Waste (from Hanford)
LLRW	Low Level Radioactive Waste
NAS	Sodium Alumino-Silicate
OGC	Offgas Reaction Chamber
REDOX	Reduction/Oxidation
SAIC	Science Applications International Corporation
SBW	Sodium Bearing Waste (from INEEL)
SPF	Studsvik Processing Facility
SRC	Solids Reaction Chamber
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
STAR	Science and Technology Applications Research center (at Idaho Falls)
THOR[sm]	THermal Organic Reduction
TRU	Transuranic Waste
TTT	THOR Treatment Technologies
WIPP	Waste Isolation Pilot Plant
XRD	X-ray Diffraction

EXECUTIVE SUMMARY

Fluidized Bed Steam Reforming (FBSR) is being considered as a potential technology for the immobilization of a wide variety of radioactive wastes, but especially aqueous high sodium wastes at Hanford, Idaho National Engineering and Environmental Laboratory (INEEL), and the Savannah River Site (SRS). To help the Department of Energy (DOE) make informed decisions about this technology for sodium bearing wastes further experimental data are needed. All work described in this study has been performed with non-radioactive simulants and compared to non-radioactive pilot scale testing at other facilities.

The desired plan is to provide a laboratory scale system that correlates to the pilot and plant scale systems such that the chemistry of Fluidized Bed Steam Reforming (FBSR) can be optimized on a small scale, then verified at the pilot scale. Once verified, this will enable laboratory scale demonstrations of actual radioactive wastes. The Savannah River National Laboratory (SRNL) developed the Bench-top Steam Reformer (BSR) to fill this need. The development of the BSR is the focus of this study. In addition, the characterization of the FBSR products produced in the BSR from simulants of the INEEL Sodium-Bearing Waste (SBW) stream and the Hanford Low Activity Waste (LAW) stream are documented and compared to pilot scale testing of these same simulants at the INEEL pilot-scale test system located at the Science Applications International Corporation (SAIC) Science and Technology Applications Research (STAR) Center in Idaho Falls, ID.

Steam reforming technology converts organic compounds primarily to CO_2 and H_2O, (with lesser amounts of H_2, CO, and other reduced gas species, depending on the operating conditions), converts nitrate/nitrite species primarily to N_2, and produces a solid residue through reactions with superheated steam, the fluidizing gas. If clay minerals are added to the process, a "mineralized" solid bed product can be produced which retains the hazardous and radioactive species. The formation of optimal mineralized species (namely feldspathoid Sodium Alumino-Silicate (NAS) type minerals with cage-like structures) is critical to maximizing the durability of the FBSR mineralized product for use as a final waste form. To form these optimal mineralized species, it is necessary to tailor the process conditions. This includes selection of appropriate additives (co-reactants such as clay), REDuction/OXidation (REDOX), process temperatures, etc. The BSR has been used to evaluate and determine process conditions at the bench-scale and have these conditions compared to the pilot scale production at the STAR Center.

An eight campaign, statistically designed matrix was performed using a nonradioactive simulant for Hanford LAW. The INEEL test matrix, using a nonradioactive simulant for the INEEL sodium bearing waste (SBW), only had a small subset of the statistical campaigns targeting more optimal conditions due to an error in the initial compositions. The statistically designed matrix recommended eight campaigns using three types of clays, two reductants, catalyst versus no catalyst, and two different operational temperatures (650°C and 725°C). One campaign for each waste type matched a STAR pilot scale campaign. The STAR pilot scale campaigns created the metastable form of nepheline (carnegieite) where the BSR formed the favored equilibrium phase of nepheline which was observed in pilot scale campaigns at Hazen Research with Hanford waste.

Statistics were applied to the Hanford eight run matrix to determine the best combination of process conditions for the destruction of offgas NO_x.

Conclusions from the performance of these campaigns are:

Use of BSR for Evaluating Steam Reformer Technology

The BSR proved to be an effective tool to evaluate treatment of wastes by the FBSR technology. The product results obtained in the BSR were generally consistent with those obtained in the THOR[sm] pilot scale runs at Hazen Research [3] and the STAR facility depending on BSR residence time. Additionally, NO_x destruction readily occurred in the BSR and a simple colorimetric system was derived to quantify NO_x destruction. The BSR proved to be a useful tool for determining appropriate conditions for larger scale FBSR operations. The BSR test results provided valuable insights into the mineralization process, in particular in areas of mineralizing stoichiometries and residence times.

CONCLUSIONS FOR INEEL SBW SIMULANT

- For the INEEL SBW, the BSR Z1 campaign with Sagger clay produced the desired nepheline phase and a related carnegieite phase during a normal 4 hour campaign; no minor or unreacted phases were observed in the final mineral products.

    ➢ These are the same phases observed in the INEEL pilot scale tests at the STAR Center

- For the INEEL SBW, the BSR Z1 campaign with Sagger clay produced the desired nepheline and sodalite phases during a 48 hour campaign, which indicates that the longer residence times (>4 hours) are needed in the BSR to stabilize nepheline and sodalite over carnegieite, e.g. the presence of metastable carnegieite indicates that all of the reactions are not complete and the residence time is too short.

- For the INEEL SBW, the BSR campaigns with Troy clay and excess NaOH produced the desired phases during 4 hour campaigns indicating that processing on the caustic side appeared to increase reactivity and mineral formation. However, excess NaOH caused an interaction between the NaOH and the CO_2 being evolved forming Na_2CO_3; this may also be caused by the REDOX stoichiometry being too low (2X vs. 3.2X) and/or the residence time being too short (only 4 hours).

- Using BB carbon with catalyst produced >98% offgas NO_x destruction. However, based on tests performed with the Hanford simulant, the same NO_x destruction could probably be attained using BB carbon with no catalyst. Offgas NO_x destruction is defined as the reduction of gaseous NO_x to N_2 and CO, and is not the % destruction of NO_x in feed solution.

CONCLUSIONS FOR HANFORD LAW SIMULANT

- For the Hanford LAW, the BSR campaigns produced the desired NAS phases, nosean (SO_4 host) and nepheline, and some less desirable metastable carnegieite in essentially all of the normal 4 hour campaigns; no minor or unreacted phases were observed in the final mineral products. Campaign H7 did not produce the metastable carnegieite.

    ➢ These were the same phases observed during pilot scale testing of the AN-107 by THOR[sm].

- In the H1-48 hour campaign, nosean and two nephelines were observed, e.g. the stoichiometric nepheline and a Na-rich nepheline and no metastable carnegieite was observed.

- The H7 campaign, reacted at the higher temperature, contained only nosean and nepheline. The H7 composition was closer to the nepheline phase region in the NAS ternary phase diagram and the phases observed in the H7 test are likely a result of this more favorable chemistry.

- The GC carbon was found to be inferior to the BB carbon and left both a carbon residue and unreacted $NaNO_3$: in some cases GC carbon preferentially stabilized Na_2CO_3 over the desired nosean/nepheline sodium aluminosilicate minerals.

- The MINCALC#3 spreadsheet used to target the BSR campaigns was verified by analyzing the H1, Z1, Z3 and Z4 products: the target and analyzed compositions matched within 1-1.5 wt% on an oxide basis.

- Statistics were applied to the eight run matrix to determine the best combination of process conditions for the destruction of offgas NO_x. Using BB carbon with no catalyst produced >98% destruction of the offgas NO_x produced which is optimum. (Note that for these experiments, no oxygen was bled into the BSR which may affect catalyst effectiveness. Also note that no difference can be detected beyond 98% destruction).

- The two temperatures of 650^oC and 725^oC had no appreciable effect on offgas NO_x destruction based on results of the colorimetric NO_x measurement technique used for these tests.

- Neither the type of clay nor the REDOXs of 1.6 versus 3.2 had an effect on the offgas NO_x destruction based on results of the colorimetric NO_x measurement technique used for these tests.

- Based on the experimental design examined in this study and the MINCALC#3 process control strategy, the H1 conditions for Hanford LAW and the Z1 conditions for INEEL SBW were recommended for testing at the STAR facility.

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1.0 INTRODUCTION

Fluidized Bed Steam Reforming (FBSR) is being considered as a potential technology for the immobilization of a wide variety of radioactive wastes, but especially aqueous high sodium wastes at Hanford, Idaho National Engineering and Environmental Laboratory (INEEL), and the Savannah River Site (SRS). To help the Department of Energy (DOE) make informed decisions about this new technology for sodium bearing wastes further experimental data are needed.

The desired plan is to provide a laboratory scale system that correlates to the pilot and plant scale systems such that the mineral chemistry, organic destruction, and NO_x destruction of Fluidized Bed Steam Reforming (FBSR) can be optimized on a small scale, then verified at the pilot scale. Once verified, this will enable laboratory scale demonstrations of actual radioactive wastes. The Savannah River National Laboratory (SRNL) developed the Bench-top Steam Reformer (BSR) to fill this need. The development of the BSR is the focus of this study. In addition, the characterization of the FBSR products produced in the BSR from simulants of the INEEL Sodium-Bearing Waste (SBW) stream and the Hanford Low Activity Waste (LAW) stream are documented and compared to pilot scale testing of these same simulants at the INEEL pilot-scale FBSR test system located at the Science Applications International Corporation (SAIC) Science and Technology Applications Research (STAR) Center in Idaho Falls, Idaho.

Steam reforming technology converts organic compounds to primarily CO_2 and H_2O (with lesser amounts of H_2, CO, and other reduced gas species, depending on the operating conditions), converts nitrate/nitrite species to primarily N_2, and produces a solid residue through reactions with superheated steam, the fluidizing gas. If clay minerals are added to the process a "mineralized" solid bed product will be produced, which retains the hazardous and radioactive species in the waste. The formation of optimal mineralized species (namely feldspathoid Sodium Alumino-Silicate (NAS) type minerals with cage-like structures) is critical to maximizing the durability of the FBSR mineralized product for use as a final waste form. To form these optimal mineralized species, it is necessary to tailor the process conditions. This includes selection of appropriate additives, REDuction/OXidation (REDOX), process temperatures, etc. The BSR has been used to evaluate and determine process conditions at the bench-scale and how these conditions compared to the pilot scale production at the STAR Center.

2.0 BACKGROUND

2.1 PREVIOUS FBSR COMMERCIAL, PILOT-SCALE, AND BENCH-SCALE EXPERIENCE

Studsvik built and tested a commercial Low-Level Radioactive Waste (LLRW) Fluidized Bed Steam Reforming (FBSR) Processing Facility in Erwin, TN, in 1997-1999 [1]. In July 1999, commercial operation of the FBSR commenced [2]. The Erwin Facility has the capability to safely and efficiently receive and process a wide variety of solid and liquid LLRW streams including: ion exchange resins, charcoal, graphite, sludge, oils, solvents, and cleaning solutions with contact radiation levels of up to 400 R/hr. The licensed and heavily Studsvik Processing Facility (SPF) can receive and process liquid and solid LLRWs with high water and/or organic content. The solid product produced is volume reduced during processing, packaged, and sent to Barnwell, SC or Envirocare, Utah for final disposal.

The Erwin facility employs the THermal Organic Reduction (THOR^{sm}) process, developed by Studsvik, which utilizes pyrolysis∗/steam reforming technology. THOR^{sm} reliably and safely processes a wide variety of LLRW's in a unique, moderate temperature (~700°C), single-stage, pyrolysis/reforming, fluidized bed treatment system. The reforming process has demonstrated effectiveness in volatilizing/oxidizing organics and separating sulfur and halogens from inorganic waste materials. Of special relevance is the capability of the THOR^{sm} technology to convert nitrates to nitrogen and sodium salts to sodium compounds that are suitable for direct disposal and/or subsequent vitrification.

In the THOR^{sm} FBSR process, a granular/particle bed material is fluidized with low pressure superheated steam. The FBSR process pyrolyzes wastes in the absence of oxygen and no combustion occurs. Therefore, the FBSR technology is Environmental Protection Agency (EPA) Clean Air Act Maximum Achievable Concentration Technology (CAA/MACT) compliant under the EPA incineration guidelines.

The THOR^{sm} FBSR technology was employed for 11 pilot scale demonstrations on high Na containing salt simulants at Hazen Research and at the STAR center [3]. The liquid waste was mixed in a batch/feed tank with selected co-reactants, including the additives necessary to make the final product into any of the following product phases (Table 1):

- Na_2CO_3 (no additives needed)
- Na_2SiO_3 (SiO_2 added)
- Na aluminosilicates (clay added)

∗ Pyrolysis chemically decomposes organic materials by heat in the absence of oxygen, e.g. C_xH_y + Heat $\rightarrow CH_4$ + C.

Table 1. THOR^{sm} Pilot Scale Demonstrations with Hanford and INEEL High Sodium Wastes

Number of Pilot Demon-strations	Additive	Mineral Product	Product Application
5	Clay	Sodium aluminosilicates such as nepheline ($NaAlSiO_4$), sodalite ($Na_6[Al_6Si_6O_{24}](2NaCl)$), and nosean ($Na_6[Al_6Si_6O_{24}](Na_2SO_4)$) that can stabilize problematic anions such as Cl, F, and SO_4	FBSR product may be acceptable as a final mineral waste form for land disposal, Yucca Mountain, Waste Isolation Pilot Plant (WIPP), etc. In small quantities the FBSR product would likely be compatible with subsequent vitrification as a frit substitute.
3	Sand or Silica	Sodium silicate	FBSR product may be acceptable as a final mineral waste form for disposal at WIPP. FBSR product may be used as a partial frit replacement in HLW melter.
3	CO_2	Sodium carbonate	FBSR product may be acceptable as a final mineral waste form for disposal at WIPP. FBSR product may be used as a partial frit replacement in HLW melter.

Several chemical and physical reactions take place in the steam reformer:

- Evaporation of all liquid

- Denitration of the nitrates and nitrites in the waste feed into nitrogen gas by the reductants added

- Conversion of organics into primarily CO_2 and H_2O, with lesser amounts of other gas species such as H_2 and CO, depending on the operating conditions

- Reduction and stabilization of hazardous metals, e.g. Cr^{+6} is reduced to a non-hazardous valence state, e.g. Cr^{+3}

- Mineralization reactions

The FBSR technology has been demonstrated to be effective at remediation of the following:

- Hanford LAW into either carbonates or silicates that can subsequently be vitrified [3]
- Hanford LAW and SRS salt supernate into a final waste form (aluminosilicate mineral) for land disposal [3, 4, 5]
- INEEL SBW into a carbonate form acceptable to WIPP as a final waste form [6] or into sodium alumino-silicate as a final waste form for land disposal.
- SRS T48 HLW supernate with tetraphenyl borate into either carbonates or silicates that are compatible with subsequent vitrification in DWPF [7, 8, 9]
- SRS Low-Curie and High-Curie salt supernates [10] into carbonate, silicate, and NAS mineral forms for burial at WIPP or Yucca Mtn.

The Savannah River National Laboratory (SRNL) has shown that the chemistry of the steam reformer product can be duplicated using staged small scale laboratory testing [7, 8, 9] in sealed crucibles. The staged small scale testing was shown to be representative of pilot scale testing [9] and thus can be used to determine process compatibility and initial conditions for larger scale testing. However, the crucible scale studies did not have the capability to capture and analyze evolved gases.

2.2 FBSR MINERAL WASTE FORM SPECIATION

The formation of mineral waste forms by FBSR has been demonstrated on an engineering scale for Hanford LAW supernates [1, 2, 3], and for INEEL SBW [11]. Different solid mineral phases are produced depending on the type of co-reactant fed with the waste, e.g. an aluminosilicate clay co-reactant produces a sodium aluminosilicate (NAS) mineral waste form comprised of nepheline ($NaAlSiO_4$), containing 8 and 9 member framework cavities that resemble cages, and other feldspathoid mineral phases, which have larger 12 membered cages that trap anion constituents such as Na_2SO_4 (nosean), NaI, NaCl (sodalite), NaF, Na_2MoO_4, Na_2TcO_4, Na_2ReO_4. The nepheline-sodalite mineral waste forms are compatible with final disposal in a Transuranic Waste (TRU) repository such as the Waste Isolation Pilot Plant (WIPP) or with final disposal by shallow land burial [4].

The NAS mineral phase assemblage(s) are anhydrous feldspathoid phases such as sodalite. The sodalite family of minerals (including nosean) are unique because they have cage-like structures formed of aluminosilicate tetrahedra. The remaining feldspathoid minerals, such as nepheline, have a silica "stuffed derivative" cage type structure. The cage structures are typical of sodalite and/or nosean phases where the cavities in the cage structure retain anions and/or radionuclides, which are ionically bonded to the aluminosilicate tetrahedra and to sodium. The cage structured feldspathoid system of minerals has the basic structural framework formula $Na_6[Al_6Si_6O_{24}]$. The square brackets in the formula are used to delineate the alumina:silica ratio of the aluminosilicate cage structure which is 1:1. The nomenclature of the minerals depends on the species inside the cage (see Table 2).

The feldspathoid mineral, sodalite, has the formula $Na_8[Al_6Si_6O_{24}](Cl_2)$. The cage is occupied by two sodium and two chlorine ions in natural sodalites [12]. The formula can also be written as $Na_6[Al_6Si_6O_{24}]\bullet(2NaCl)$ to indicate that two NaCl are ionically bonded in the cavities of the cage structure, while the remaining Na:Si:Al have a 1:1:1 stoichiometry [12]. When the 2NaCl are replaced by Na_2SO_4, the mineral phase is known as nosean, $(Na_6[Al_6Si_6O_{24}](Na_2SO_4))$ which is one of the feldspathoid cage structured minerals found in the FBSR waste form. Since the Cl^-, $SO_4^=$, and/or S_2 are chemically bonded inside the sodalite cage structure, these species do not readily leach out of the respective FBSR waste form mineral phases.

Other minerals in the sodalite family, namely hauyne and lazurite, which are also cage structured minerals, can accommodate either SO_4 or S_2 depending on the REDOX of the sulfur during the steam reforming process. Regardless of the FBSR REDOX, the feldspathoid minerals can accommodate sulfur as either sulfate or sulfide. Sodalite minerals are known to accommodate Be in place of Al and S_2 in the cage structure, along with Fe, Mn, and Zn, e.g. helvite $(Mn_4[Be_3Si_3O_{12}]S)$, danalite $(Fe_4[Be_3Si_3O_{12}]S)$, and genthelvite $(Zn_4[Be_3Si_3O_{12}]S)$ [21]. These cage-structured sodalites were minor phases in HLW supercalcine waste forms∗ [13] and were found to retain Cs, Sr, and Mo in the cage-like structure, e.g., Mo as $Na_6[Al_6Si_6O_{24}](NaMoO_4)_2$ [13]. In addition, sodalite structures are known to retain B[14], Ge[15], I[15,21] and Br[15,21] in the cage-like structures. Indeed, waste stabilization at Argonne National Laboratory-West (ANL-W) currently uses a glass-bonded sodalite ceramic waste form (CWF) for disposal of electrorefiner wastes for sodium-bonded metallic spent nuclear fuel from the EBR II fast breeder reactor [16,17].

A second feldspathoid mineral found in the FBSR waste form is nepheline $(NaAlSiO_4)$ [18]. Nepheline is a hexagonal structured feldspathoid mineral (see Table 2). The cage structured aluminosilicate framework of nepheline forms cavities within the framework. There are eight large (nine-fold oxygen) coordination sites and six smaller (8-fold oxygen) coordination sites [21]. The larger nine-fold sites can hold large cations such as Cs, K, and Ca, while the smaller sites accommodate the Na. The K analogue is known as leucite $(KAlSi_2O_6)$. In nature, the nepheline structure is known to accommodate Fe, Ti, and Mg as well.

The remaining aluminosilicate mineral found in the FBSR waste form is a sodium rich cubic structured nepheline derivative $(Na_2O)_{0.33}Na[AlSiO_4]$ (PDF#39-0101). This nepheline derivative structure has large (twelve-fold oxygen) cage like voids in the structure [19]. This cage structured nepheline is not known to occur in nature, but the large cage like voids should be capable of retaining large radionuclides, especially monovalent radionuclides such as Cs.

∗ Supercalcines were the high temperature silicate based "natural mineral" assemblages proposed for HLW waste stabilization in the United States (1973-1985).

Carnegeite (Table 2) is a metastable form of nepheline that usually forms due to insufficient reaction. Carnegeite has a similar structure to nepheline, but readily transforms to nepheline upon heating or longer reaction time. While carnegeite can have an Al:Si ratio of 1:1 it is also capable of forming a variety of mineral structures that are either Si or Al deficient (see Table 2).

Table 2. Feldspathoid Minerals Commonly Found in FBSR

Substitution In Cage Structure	Chemical Formula	Common or Mineral Name	Density (g/cm3)	Crystal Type	Ref.
Precursor					
NONE	$Na_{12}[Al_{12}Si_{12}O_{48}] \bullet 27H_2O$	Zeolite-A	$1.99^‡$	Cubic	20, 22
Nephelines and Stuffed Cristobalites					
UNKNOWN	*(K,Na)AlSiO₄*	Nepheline	2.63	Hexagonal	PDF#35-424
UNKNOWN	$NaAlSiO_4$	Carnegieite	2.401	Cubic	PDF #11-221
UNKNOWN	*(Na₂O)₍≤0.33₎NaAlSiO₄*	Na rich Nepheline	2.64	Cubic	PDF #39-101
UNKNOWN	$Na_{1.45}Al_{1.45}Si_{0.55}O_4$	Na-Al Carnegieite	2.62	Cubic	PDF #49-2
UNKNOWN	$Na_{1.95}Al_{1.95}Si_{0.05}O_4$	Na-Al Carnegieite	2.72	Tetragonal	PDF # 49-3
UNKNOWN	$Na_{1.75}Al_{175}Si_{0.25}O_4$	Na-Al Carnegieite	2.72	Orthorhombic	PDF # 49-4
UNKNOWN	$Na_{1.65}Al_{165}Si_{0.35}O_4$	Na-Al Carnegieite	2.69	Tetragonal	PDF # 49-5
UNKNOWN	$Na_{1.55}Al_{155}Si_{045}O_4$	Na-Al Carnegieite	2.674	Orthorhombic	PDF # 49-6
UNKNOWN	$Na_{1.15}Al_{115}Si_{085}O_4$	Na-Al Carnegieite	2.578	Orthorhombi	PDF # 49-7
UNKNOWN	$Na_3MgAlSi_2O_8$	Na-Mg Carnegieite	Not given	Orthorhombi	PDF # 49-8
Sodalite Group					
2NaCl	$Na_6[Al_6Si_6O_{24}](2NaCl)$	Sodalite	2.31^*	Cubic*	21
2NaOH	$Na_6[Al_6Si_6O_{24}](2NaOH) \bullet 1.5H_2O$	Basic Sodalite or Hydroxysodalite	2.215^{**}	Cubic**	22
2NaNO₃	$Na_6[Al_6Si_6O_{24}](2NaNO_3)$	Nitrated Sodalite	2.342	Cubic	PDF#50-0248
Na₂SO₄	*Na₆[Al₆Si₆O₂₄](Na₂SO₄)*	Nosean	2.21^{tt}	Cubic^{tt}	23
xNaOH + y H₂O	$Na_6[Al_6Si_6O_{24}](xNaOH) \bullet yH_2O$	Basic Nosean			22
1-2(Ca,Na)SO₄	$(Na)_6[Al_6Si_6O_{24}]((Ca,Na)SO_4)_{1-2}{}^t$	Hauyne	2.4^t	Cubic^t	23
x(Ca,Na)(S,SO₄ ,Cl)	$(Ca,Na)_6[Al_6Si_6O_{24}]((Ca,Na)S,SO_{4,}Cl)_x{}^t$	Lazurite	2.43	Cubic	PDF #17-749
Cancrinite Group					
2NaNO₃	$Na_6[Al_6Si_6O_{24}](2NaNO_3) \bullet 4H_2O$	Nitrated Cancrinite	2.51	Hexagonal	PDF #38-513
(Na,Ca,K)₂CO₃	$(Na,Ca,K)_6[Al_6Si_6O_{24}]((Na,Ca,K)_2CO_3)_{1.6} \bullet 2.1H_2O$	Cancrinite	2.60	Hexagonal	PDF #25-776
2(Na, K)Cl	$(Na,Ca,K)_6[Al_6Si_6O_{24}](2(Na,K)Cl)_{2-3}$	Microsommite	2.34	Hexagonal	PDF #20-743
2(Na, K)Cl	$(Na,Ca,K)_6[Al_6Si_6O_{24}]((Na,K)_2SO_4,Cl)_3$	Davyne	2.46	Hexagonal	PDF #20-379
Na₂CO₃	$Na_6[Al_6Si_6O_{24}](Na_2CO_3)$	Natrodavyne	Not given	Hexagonal	PDF #15-794

t	PDF #20-1087	* PDF # 20-495	‡ PDF #11-0590 and #38-241
tt	PDF #17-538	** PDF #11-401	

Phases in italics are the phases found in the THOR[sm] demonstration [3]

3.0 APPROACH

The objectives of this work were to design, build, and test the BSR, and perform campaigns with Hanford LAW and INEEL SBW simulants. The BSR was designed to operate with the same temperature, low pressure, and superheated steam atmosphere as a FBSR. Though the BSR was not a fluidized bed, it could produce the same offgas NO_x destruction as an FBSR by having a second reaction chamber in which the offgases were forced to flow and react with previously formed mineral product and carbon. The BSR also has the flexibility to control the residence time of the product under reaction conditions. The test conditions for each campaign were derived from a statistical design. The design recommended an eight run matrix of process conditions using a variety of clays, reductants, and catalysts at two different operational temperatures (650°C and 725°C). One campaign for each waste type matched a STAR pilot scale campaign. The STAR pilot scale campaigns created the metastable form of nepheline (carnegieite) where the BSR formed the favored equilibrium phase of nepheline which was observed in pilot scale campaigns at Hazen Research with Hanford waste.

The products produced in the BSR were characterized by whole element chemical compositional measurements and x-ray diffraction (XRD). Product durability was measured via the Product Consistency Test (PCT), ASTM C1285.02 and these results are reported elsewhere. Samples with different residence times in the BSR and/or at temperature were also tested and compared to optimize the residence time in the BSR to be consistent with the INEEL pilot scale testing. All of the analyses performed in the BSR provide data for comparison to the INEEL pilot-scale testing.

4.0 EXPERIMENTS

4.1 BENCH-TOP STEAM REFORMER AND PRODUCT DESCRIPTION

The BSR designed at SRNL is a two-stage unit used to produce the same mineralized products and gases as a FBSR. A schematic of the unit designed is shown in Figure 1.

Figure 1. Schematic of Bench-top Steam Reformer
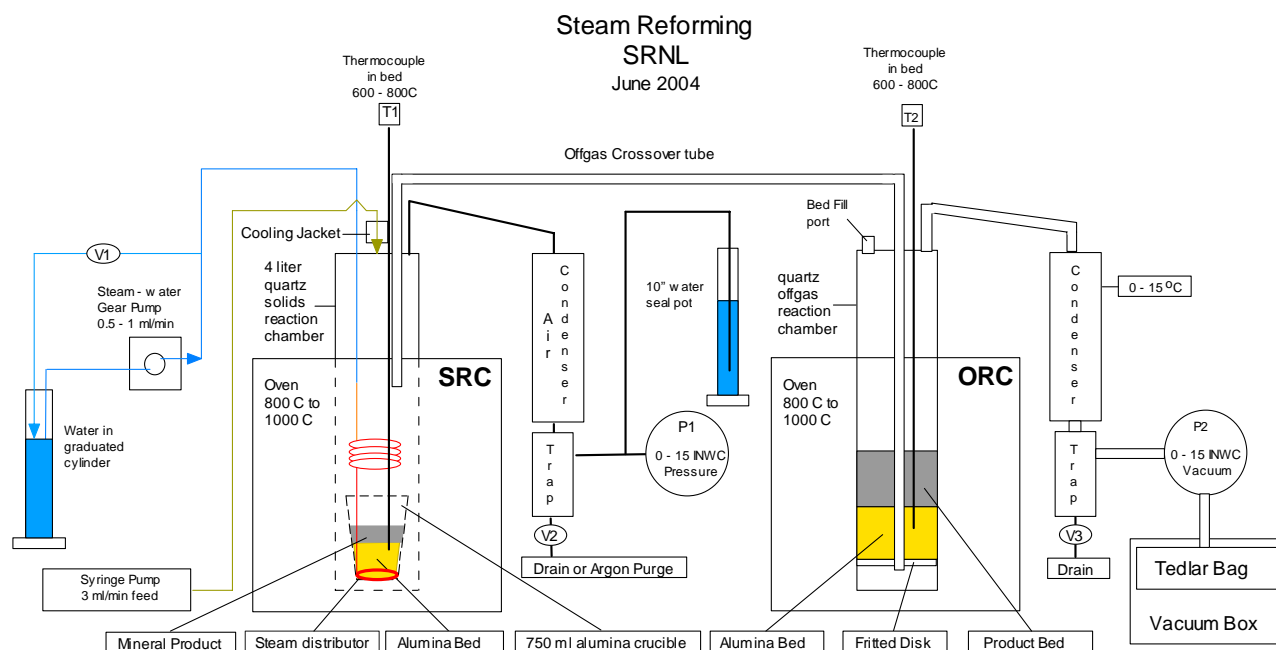
The solids reaction chamber (SRC), which simulates the FBSR bed, holds a crucible into which a steam distributor, submerged in an alumina bed, is used to produce the superheated steam needed for the reactions. The premixed feed slurry is dripped into the crucible where the reactions take place. The SRC is operated at the desired temperature at near ambient pressure.

The premixed feed slurry contains a waste simulant, a reductant, a catalyst (if desired), and a co-reactant (in this study, a clay). The Na_2O, Al_2O_3, and SiO_2 concentrations of the simulant and of the particular clay are used to proportion the simulant with the clay such that the right ratios of these components are available to form the desired product stoichiometry. Since different clays have different ratios of Al:Si and the different simulants have different ratios of Na:Al, the type of clay used allows tailoring of the product chemistry. Figure 2 shows the ternary phase diagram that can be used to target the correct feldspathoid mineral stoichiometry for sodium bearing wastes. The symbol in the center of the ternary plot corresponds to the actual product chemistries tested in the Hanford LAW campaigns.

Figure 2. Na$_2$O-Al$_2$O$_3$-SiO$_2$ Ternary Phase Diagram
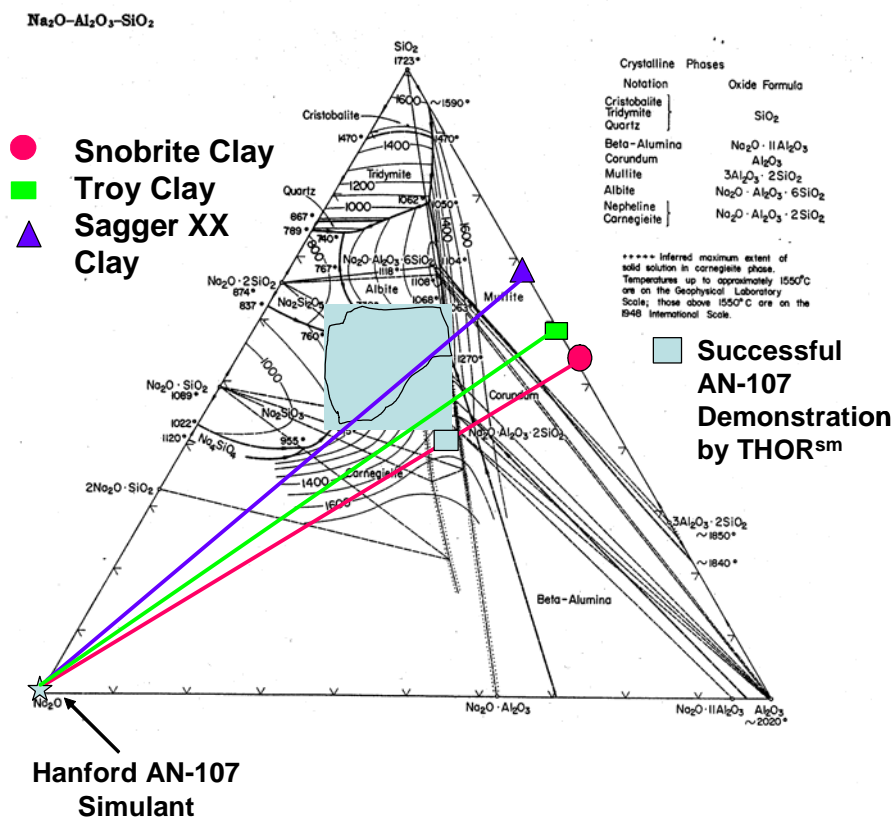
The feed slurry also contains a carbon reductant additive. The carbon reacts with the steam to produce hydrogen and together they react with NO$_x$ gases to produce N$_2$, CO, and CO$_2$. The catalyst may be added to aid in the NO$_x$ reduction. Though excess carbon or catalyst won't adversely affect the process, they are normally added at the minimum necessary amounts to reduce costs of operation.

Initially, the feed droplets collide with an alumina starting bed which is partially fluidized by the flow of steam in the crucible until a fritted disk of product and alumina is created. Once the fritted disk completely covers the area above the alumina, fluidization of the alumina ceases. From this point on, a monolith of product forms on top of the fritted disk, which may have a gray interior, likely due to incomplete reaction from the lack of fluidization, and a white exterior. Figure 3 shows the product from a Hanford run.

Figure 3. Product Form in BSR

The mineralized products in the porous product disk are the same as those in the white part of the monolith. The porous product disk however, also contains a significant amount of alumina bed material. The center or gray part of the monolith usually has unreacted feed material that is not found in the porous product disk or in the white exterior of the monolith. A large part of the unreacted feed material in the center of the monolith is carbon. Subsequent roasting in air at 650°C for 3 hours can be used to remove this unreacted carbon, and this does not change the mineralogy of the product.

Gases and steam leaving the crucible travel through an insulated crossover tube and into the second stage of the unit, the Offgas Reactor (OGC). In the OGC, the gases go through more heated alumina startup bed material before reacting with ground up mineral product that comes from a previous run. Early tests in a single unit BSR did not reduce the NO_x gases. The NO_x must come in contact with the solid carbon, which is in the mineral product, in order to be reduced to N_2. Though carbon alone is all it takes for the reduction to occur, using product is closer to simulating the FBSR conditions. The resulting steam is condensed and collected in a trap and the non-condensable gases are dried through desiccant before being collected in a Tedlar bag for analysis. Figure 4 shows a picture of the BSR. The Tedlar bag in the vacuum box is not in view. Figure 5 shows the Tedlar bag in the vacuum box.

Figure 4. BSR Photograph

Figure 5. Tedlar Bag in Vacuum Box

4.2 INEEL SBW SIMULANT MAKEUP

The laboratory results for the SBW simulant versus target values are shown in Table 3. The phosphate was added after the analysis was performed, so the phosphate concentration reflects the expected concentration based on the amount added. The measured pH of the simulant was 1.30.

Table 3. SBW Simulant Concentrations

Ion	Analyzed mg/L	Target mg/L
Al	17900	18000
B	N/A	120
Ca	2100	1800
Cr	N/A	170
Cs	N/A	260
Cu	N/A	44
Fe	1080	1210
K	9550	7700
Mg	275	290
Mn	795	780
Na	46500	47000
Ni	N/A	86
Re	N/A	120
Zn	N/A	69
NO_3	357000	335000
PO_4	(2200)	2200
SO_4	8090	8040
F	N/A	900
Cl	N/A	1000
I	N/A	15

N/A = Not Analyzed. Only major cations and anions were measured to cross-check simulant makeup.

4.3 HANFORD LAW SIMULANT MAKEUP

The laboratory results for the LAW simulant versus the target values are shown in Table 4. The measured pH of the simulant was 12.91.

Table 4. LAW Simulant Concentrations

	Analyzed 1L Hanford LAW mg/L	Analyzed 3L Hanford LAW mg/L	Target Hanford LAW mg/L
F	583	573	600
I	N/A	1.1	1.7
Cl	1560	1590	1530
NO_2	18600	19300	19500
NO_3	157000	161000	155600
PO_4	4310	4420	4674
SO_4	8720	8910	8640
Al	1870	1900	1720
Cr	517	528	540
Cs	N/A	0.26	0.01
K	936	912	484
Na	114000	114000	115000
Re	N/A	73.7	96.0

N/A Not Analyzed. Minor components were only measured in the 3-liter batch.

4.4 HANFORD AN-107 SIMULANT MAKEUP

The laboratory results for the LAW simulant versus the target values are shown in Table 5.

Table 5. AN-107 Simulant Concentrations

Slurry Analyte	Analyte Target Composition mg/L	Analyte Analzyed Composition mg/L	Raw Chemical	Amount Required, lbs/Batch
Al	5.12E+03	5.43E+03	$Al(NO_3)_3 \bullet 9H_2O$	3,235.95
Ca	4.23E+02	9.00E+02	$Ca(NO_3)_2 \bullet 4H_2O$	67.22
Cr	2.26E+02	2.00E+02	$Na_2CrO_4 \bullet 4H_2O$	27.4
Cs	1.07E+01	0.00	$CsNO_3$	0.42
Fe	2.07E+03	1.86E+03	$Fe(NO_3)_3 \bullet 9H_2O$	400.95
K	1.21E+03	2.23E+03	KOH	54.70
La	2.59E+01	2.10E+01	La_2O_3	0.82
Na	1.85E+05	1.73E+05	NaOH, 50% sol.d=1.53	5,656.39
Ni	3.64E+02	3.00E+00	NiO	12.38

Pb	2.94E+02	2.07E+02	PbO	8.47
Re			NaReO$_4$ (spike added by Hazen)*	0.0233
Cl	1.38E+03	1.51E+03	NaCl	61.42
F	2.49E+03	4.10E+03	NaF	148.47
PO$_4$	2.71E+03	NA	Na$_3$PO$_4$•12H$_2$O	292.13
SO$_4$	7.86E+03	3.84E+03	Na$_2$SO$_4$	313.69
NO$_2$	4.47E+04	4.77E+04	NaNO$_2$	1,845.05
NO$_3$	1.57E+05	1.66E+05	NaNO$_3$	4,157.71
CO$_3$	5.40E+04	NA	Na$_2$CO$_3$	2,546.64
TOC			Na$_2$EDTA.2H$_2$O	222.88
			Na$_3$HEDTA.2H$_2$O	662.16
			Sodium Acetate	261.03
			Sodium Formate	327.72
			Sodium Oxalate	165.12
			Sodium Gluconate	162.67
			Glycolic Acid	640.98
			Nitrilotriacetic Acid	186.22
			Citric Acid	542.23
			Iminodiacetic Acid	175.30
			Water	14,590.44
			Slurry Volume, gal	3,200

4.5 STATISTICAL OPERATING CONDITIONS MATRIX

The conditions for each run originated from a statistical design. The design recommended eight different run conditions. The operating conditions test matrix is shown in Table 6.

Table 6. Operating Conditions Test Matrix

Temperature (°C)	REDOX Stoichometry	Catalyst	Clay	Carbon
725	+	yes	Clay 1	BB
650	+	yes	Clay 1	GC
725	+	yes	Clay 2	GC
725	-	yes	Clay 1	GC
650	-	no	Clay 2	BB
650	+	no	Clay 1	BB
725	+	no	Clay 3	GC
650	-	yes	Clay 3	BB

For the INEEL SBW campaigns:
Clay 1 = Troy, Clay 2 = Sagger, Clay 3 = OptiKast.

For the Hanford LAW Campaigns:
Clay 1 = OptiKast, Clay 2 = Sagger, Clay 3 = Troy.

The analysis of the clays, carbon, and SpherOx catalyst are given in reference 24.

For each type of waste, clay 1 was postulated to be the clay of choice to optimize the Na_2O, Al_2O_3, and SiO_2 concentrations to make the feldspathoid minerals nepheline-sodalite-nosean.

The REDOX column in Table 6 refers to a factor times the stoichiometric carbon addition required to reduce the NO_x gases to N_2. The "+" was a factor of 3.2X the stoichiometric amount needed to reduce all NO_2 and NO_3 to N_2 and the "−" was a factor of 1.6X the stoichiometric amount needed to reduce all NO_2 and NO_3 to N_2 for the LAW campaigns. For the SBW campaigns the "+" was a factor of 3.2X and the "−" was a factor of 2X the stoichiometric amount needed to reduce all NO_2 and NO_3 to N_2.

The actual operating conditions for all the campaigns performed are shown in Table 7.

Table 7. Operating Conditions for Steam Reforming Campaigns

Run	Date	Temperature (°C)	REDOX Stoichiometry	Catalyst	Clay	Waste Loading	Excess NaOH	Carbon*
INEEL SBW CAMPAIGNS (4 HOUR)								
C1	7/15/04	725	3.2	yes	Troy	30	no	BB
C2	7/19/04	650	3.2	yes	Troy	30	no	GC
C3	7/21/04	725	3.2	yes	Sagger	30	no	GC
Z1	7/27/04	725	2	yes	Sagger	38	no	BB
Z2a	8/23/04	725	2	yes	Troy	35	yes	BB
Z3	8/18/04	725	2	yes	Troy	38	no	BB
Z4	8/16/04	725	2	yes	Troy	31	yes	BB
HANFORD LAW CAMPAIGNS (4 HOUR)								
H1	7/27/04	725	3.2	yes	OptiKast	23	no	BB
H2	7/29/04	650	3.2	yes	OptiKast	23	no	GC
H3	8/3/04	725	3.2	yes	Sagger	23	no	GC
H4	8/4/04	725	1.6	yes	OptiKast	23	no	GC
H5	8/10/04	650	1.6	no	Sagger	23	no	BB
H6	8/24/04	650	3.2	no	OptiKast	23	no	BB
H7	9/7/04	725	3.2	no	Troy	23	no	GC
H8	9/8/04	650	1.6	yes	Troy	23	no	BB
HB	8/12/04	725	0	no	OptiKast	23	no	None
HANFORD AND SBW CAMPAIGNS (48 HOUR)								
Z1-48 hr	9/21/04	725	2	yes	Sagger	38	no	BB
H1-48 hr	9/27/04	725	3.2	yes	OptiKast	23	no	BB

The campaigns denoted with a "C" or "Z" treated INEEL SBW simulant. The first three campaigns of this matrix were denoted as campaigns C1, C2, and C3 and the waste loading was kept at a constant 30 wt% on a dry calcine oxide/anion basis. By the end of run C3, it was realized that a mistake was made in the clay to waste ratio calculation. By using the information obtained in the "C" campaigns, a reduced matrix of campaigns, denoted as Z1 through Z4, was performed. The mistake in the batching sheets had prevented waste loadings of >30 wt% for the SBW waste, but the revised calculations indicated that waste loadings as high as 38 wt% could be achieved in the absence of additional NaOH neutralization of the acidic SBW (see Table 7 and discussion below).

The campaigns denoted "H" treated Hanford LAW simulant. Campaigns H1 through H8 followed the prescribed eight run matrix. Run HB was a special baseline run which excluded carbon and catalyst for the purpose of determining the color concentration of NO_x, assuming that in the absence of carbon no NOx had been reduced to N_2.

INEEL run Z1 and Hanford run H1 were both repeated and kept in the steam reformer for 48 hours after completion of feeding to determine if the short residence times, e.g., 4 hours, were inadequate to make well reacted product. This was done to react the excess carbon and to provide additional residence time to facilitate further reaction of the product (i.e., to be more prototypical of actual FBSR operation, which has a much longer particle residence time).

4.6 STEAM REFORMER FEED MAKEUP

4.6.1 INEEL SBW Feed Makeup

A typical batch was based on 120 grams of clay. The ratio of grams simulant to grams clay from MINCALC #3 spreadsheet was used to calculate the appropriate grams of simulant for 120 grams of clay. Appendix A contains a MINCALC #3 spreadsheet. The volume of the clay and waste times a factor from MINCALC determined the grams of carbon added based on the following equations:

$$1C + 0.8NaNO_3 = 1CO_2 + 0.4Na_2O + 0.4N_2$$

$$1C + 1.33NaNO_2 = 1CO_2 + 0.66Na_2O + 0.66N_2$$

The amount of catalyst added was 5% of the total weight of all other components in solution, with the exception of the dilution water. Dilution water was added to run Z2a to change the viscosity from that of a high viscosity material (similar to axle grease) to a smooth flowable liquid.

Campaigns Z2a and Z4 had NaOH added to neutralize the acidic SBW for enhanced reactivity with the clay as determined in a separate study [24]. The waste to clay ratio was first used to determine the total amount of waste to add. The sum of the 50 wt% NaOH solution and waste simulant equaled the total waste to add to the clay.

For run Z2a, enough NaOH was added to the waste simulant in order to double the molar Na concentration. This made for a thick solution that had the consistency of axle grease. Its measured pH was 8.05. In this pH regime the aluminum present in the waste would tend to form hydroxide species, thus increasing viscosity. Dilution water was later added to this solution to make it flowable.

Prior to run Z4, a series of experiments was performed by adding 50 wt% NaOH solution to waste simulant, measuring the pH, and then observing the flow characteristics both immediately and approximately one hour later. It was found that the flow did not significantly improve until the pH > 13.2 when $Al(OH)_3$ solubilizes as AlO_2^-. In order to reach that level of pH, 5.924 grams of 50 wt% NaOH was added to 20 grams of waste simulant. Thus, the ratio of 5.924g:20g caustic:simulant was used to determine how much caustic to add to run Z4.

The waste to clay ratios, listed in Table 8, determine where the product will lie on the SiO_2, Na_2O, Al_2O_3 ternary phase diagram (Figure 2). A spreadsheet error (MINCALC #1) was found after campaigns C1 through C3 were processed in the BSR. This placed the C1, C2, and C3 products in a less desirable region of the ternary phase diagram. The error was corrected (MINCALC #3) and campaigns Z1 through Z4 reflect the correction.

Table 8. INEEL SBW Steam Reformer Batch Makeup

RUN	Clay (grams)	g waste/ g clay	Waste (grams)	NaOH (grams)	Carbon (grams)	Catalyst (grams)	DI Water (grams)
C1	120	3.29	394.67	0.00	102.9	30.88	0.00
C2	120	3.29	394.67	0.00	102.9	30.88	0.00
C3	120	3.38	405.85	0.00	105.13	31.55	0.00
Z1	60	5.82	349.12	0.00	51.83	23.05	0.00
Z2a	60	3.37	179.43	22.99	33.24	13.12	52.51
Z3	120	5.66	679.08	0.00	101.23	39.95	0.00
Z4	120	2.38	220.65	65.36	51.44	20.30	0.00
Z1 (48)	60	5.82	349.12	0.00	51.83	23.05	0.00

For campaigns Z2a and Z4, the g waste in the g waste/g clay ratio is considered the sum of the g waste + g NaOH.

4.6.2 Hanford LAW Feed Makeup

A typical batch was based on 120 grams of clay. A ratio of grams waste to grams clay was used from a MINCALC spreadsheet to calculate grams of waste. Appendix A contains a MINCALC #3 spreadsheet. The volume of the clay and waste times a REDOX ratio factor , e.g., 2X or 3.2X the amount of stoichiometric NO_3 and NO_2 based on the equations given in section 4.5.1 from MINCALC, determined the grams of carbon added. The amount of catalyst added was 5% of the total weight of all other components in solution, with the exception of the dilution water. Dilution water was added to all Hanford campaigns to reach a 600 gram batch size with 120 grams clay. Table 9 shows the Hanford LAW steam reforming batch makeup.

Table 9. Hanford LAW Steam Reformer Batch Makeup

RUN	Clay (grams)	g waste/ g clay	Waste (grams)	Carbon (grams)	Catalyst (grams)	DI Water (grams)
H1	120	1.95	234.37	37.43	19.59	188.61
H2	120	1.95	234.37	36.98	19.57	189.08
H3	120	2.02	242.04	37.78	19.99	180.19
H4	120	1.95	234.37	18.49	18.64	208.49
H5	120	2.02	242.04	19.35	0.00	218.61
H6	120	1.95	234.37	37.43	0.00	208.20
H7	120	1.96	235.41	37.09	0.00	207.51
H8	120	1.96	235.41	18.77	18.71	207.12
HB	60	1.95	117.19	0.00	0.00	122.81
H1-(48)	60	1.95	117.18	18.71	9.79	28.5

4.7 OFFGAS BED CREATION

Seventy-five percent of each batch was made into product which was later added to the offgas reactor. The product was ground and sieved through a 12 mesh screen before it was added atop the alumina. Figure 6 shows a typical ground product added to the offgas reaction chamber.

Figure 6. Ground Steam Reformer Product for Offgas Reaction Chamber

The quantities of product (with residual carbon) used for the offgas bed and the amount of feed it took to produce it are shown in Table 10. Offgas analysis was not performed on campaigns Z1, Z2, Z1-48hr, HB, and H1-48hr.

Table 10. Product for Offgas Bed

Run	Amount fed (grams)	Product formed (grams)
C1	433.98	150
C2	445.64	161.1
C3	450.01	173
Z3	704.5	148.3
Z4	330.6	115.3
H1	412.14	unknown
H2	445.26	128
H3	450.24	133.3
H4	450.11	109.1
H5	450.5	112.1
H6	409.5	110.5
H7	450	107.7
H8	451	108

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The feed to product formed ratio for campaign Z-3 was much greater than all the other runs because it had a large amount of NaOH added to it to raise the pH. A portion of the formed product was also taken for x-ray diffraction (XRD) analysis (see section 5.1 discussion).

4.8 OFFGAS GENERATION AND CAPTURE

The following day, after creating the offgas bed product, the system was reheated to temperature and the last twenty five percent of the original feed was fed to the steam reformer. A 20-liter Tedlar bag was attached downstream of the condenser and desiccant in order to collect all non-condensable gases. At the end of the run, the bag was submerged in water with a pressure gauge attached and the volume of the gas at room temperature was determined. The volume of gases collected in the bag for each run is shown in Table 11.

Table 11. Gas Volumes from Steam Reforming Campaigns

Run	Amount fed for gas analysis (grams)	Volume of gas produced (liters)
C1	60.22	12.19
C2	74.83	9.16
C3	88.41	11.29
Z3	43.94	15.49
Z4	49.45	14.88
H1	76.81	10.45
H2	109.83	8.42
H3	99.95	7.00
H4	112.34	5.04
H5	103.12	4.81
H6	161.49	11.94
H7	114.53	13.45
H8	106.73	4.29

Immediately after determining the gas volume, a sample of the gas was withdrawn with a syringe and immediately analyzed by a gas chromatograph. The remainder of the gas was blown through a 52 millimeter diameter tube and the color was matched to Dutch Boy paint color charts. This was done to get a semi-quantitative comparison of the NO_x destruction between campaigns (methodology is described below).

4.9 PRODUCTS FROM CAMPAIGNS WITH NO OFFGAS ANALYSIS

Campaigns Z1, Z2, Z1-48hr, HB, and H1-48hr did not have offgas analyses performed on them. The interest was only in the solid product. For these campaigns, feed makeup was based on a 60 gram clay batch as shown in Table 8 and
Table 9. Table 12 shows the mass of feed versus the mass of product formed for these campaigns.

Table 12. Feed versus Product Mass for Solids Only Campaigns

Run	Amount fed (grams)	Product formed (grams)
Z1	435.2	99.5
Z2	296.6	60.0
Z1-48hr	431.1	81.5
HB	282.3	66.7
H1-48hr	201.0	60.2

5.0 ANALYSIS & OBSERVATIONS

5.1 SOLID PHASE PRODUCTS

5.1.1 INEEL SBW Solid Phase Products

All of the products were a uniform dark gray in color except for run Z1-48hr. The dark gray color was due to unreacted carbon in the product during the normal 4 hour residence time in the BSR. However the Z1 product that had a 48 hour residence time in the BSR was a uniform tan color as shown in Figure 7 indicating that the longer residence time was needed for complete carbon consumption.

Figure 7. Z1-48hr Product

The form of the BSR INEEL SBW steam reformed products was the same as the Z1-48hr product shown in Figure 7. The color (either dark gray or tan) of the BSR INEEL SBW steam reformed products was nearly uniform throughout as shown in Figure 8.

Figure 8. Z1-48hr Product Interior

The x-ray diffraction (XRD) results of the product phases produced are given in Table 13 . The cage structured sodalite (Cl and F host phase) and nosean (SO$_4$ host phase) were not observed in any of the 4-hour BSR products, but were observed in the 48 hour BSR product. Nepheline was observed in all of the 4 hour and the 48 hour products. The location of the different clay and SBW simulant mixtures from Table 7 are shown on the Na$_2$O-Al$_2$O$_3$-SiO$_2$ ternary diagram in Figure 9. The XRD analyses can be interpreted in terms of the compositional similarity of a particular campaign to the composition of the successful Hanford AN-107 campaign performed by TTT [3] as indicated by the square in Figure 9.

The BSR campaigns C1, C2, and C3 were not located in the region of the phase diagram closest to the AN-107 campaign because of the mistake in the original MINCALC spreadsheet (ovals and diamond in Figure 9). These campaigns did not produce the desired nepheline phase, but produced the metastable nepheline known as carnegieite (Table 13). Unreacted SiO$_2$ from the clay was present in significant quantities, as these mixtures were too clay rich and contained magnetite (Fe$_3$O$_4$) from catalyst that was not completely reacted. These campaigns did demonstrate that the GC carbon was less reactive than the BB carbon and produced more unreacted amorphous carbon residue as shown by the XRD analyses.

The BSR campaign Z-1 (4 hour and 48 hour, see triangle in Figure 9) were located very close to the successful AN-107 campaign. Both the 4 hour and the 48 hour campaigns produced the desired phases at a calcined waste loading of 38 wt%. The 4 hour campaign produced the desired nepheline and some additional carnegieite (Table 13). The 48 hour campaign produced the cage structured nepheline and sodalite and a mineral that also has a cage like structure known as combeite. No carnegieite was found in the 48 hour campaign, indicating that all carnegieite has transformed to the stable nepheline phase with the longer residence times. This mixture of Sagger clay with SBW simulant was recommended for further testing in the INEEL STAR facility pilot scale FBSR.

BSR campaign Z2a was a mixture of Troy clay and SBW simulant that had been pH adjusted by the addition of 2M of NaOH.   The Z2a BSR campaign is indicated by the hexagon in Figure 9. It is also close to the successful AN-107 TTT campaign and produced the desired phases, nepheline and some carnegieite. This campaign proved that extra NaOH could be added to the SBW and a different clay used to target the AN-107 region of the ternary phase diagram. This mixture produced a 35 wt% waste loading, as the NaOH is considered an additional mineralizing additive, but similar product phases to the SBW/Sagger clay Z1 campaign at a 38 wt% waste loading were produced.

BSR campaign Z3 was a mixture of Troy clay and unadjusted SBW simulant. This campaign was performed to compare it to the Z1 campaign with unadjusted SBW simulant and Sagger clay. The Z3 mixture was calculated at the same waste loading (38 wt%) as the Z1 campaign and this put the campaign in a higher temperature (less desirable) region of the phase diagram (see doughnut shape in Figure 9). While the desired nepheline phase was made, there was more of the metastable carnegieite.

BSR campaign Z2a was a mixture of Troy clay and SBW simulant that had been pH adjusted by the addition of 3M of NaOH.   The Z4 BSR campaign is indicated by the cross in Figure 9. It is also close to the successful AN-107 TTT campaign and produced the desired phases, nepheline and some carnegieite. However, the extra NaOH (over that used for the Z2a campaign) appears to have reacted with the BB carbon used to form Na_2CO_3 leaving some unreacted nitrated or nitrited feldspathoid minerals (cancrinite). This may be because a REDOX stoichiometry of 2 was used instead of 3.2 for this campaign or because of the shorter residence time of the BSR (4 hours vs. 48 hours in FBSR).

In the Z2a, Z3, and Z4 campaigns minor phases such as magnetite from unreacted catalyst, TiO_2 impurities from the Troy clay [24] and SiO_2 from the clay were also present. Because the catalyst and TiO_2 are randomly distributed throughout the samples some XRD patterns showed the presence of these species and some samples did. In some cases Al_2O_3 from the startup bed was also present.

Table 13. Solid Phases Identified in SWB BSR Campaigns by X-Ray Diffraction (XRD) Without Roasting

Sample ID	Type of Clay	Type of Carbon	Temp ^oC	Major Phases	Minor Phases
C1	Troy	BB	725	carnegieite ($NaAlSiO_4$) nepheline ($NaAlSiO_4$) Quartz (SiO_2)	Al_2O_3
C2	Troy	GC	650	carnegieite ($NaAlSiO_4$) Quartz (SiO_2) Magnetite (Fe_3O_4)	Al_2O_3 amorphous carbon
C3	Sagger	GC	725	carnegieite ($NaAlSiO_4$) Nepheline ($NaAlSiO_4$) Quartz (SiO_2)	Magnetite (Fe_3O_4)
Z1	Sagger	BB	725	Na rich Nepheline ($K_{0.12}Na_{0.87}Al_{0.99}Si_{1.01}O_4$) Na-Al Carnegieite ($Na_{1.55}Al_{1.55}Si_{0.45}O_4$)	None
Z2a	Troy	BB	725	Na rich Nepheline ($K_{0.12}Na_{0.87}Al_{0.99}Si_{1.01}O_4$) Na-Al Carnegieite ($Na_{1.55}Al_{1.55}Si_{0.45}O_4$)	Magnetite (Fe_3O_4) Anatase (TiO_2) Cristobalite (SiO_2)
Z3	Troy	BB	725	Na rich Nepheline ($K_{0.15}Na_{0.75}Al_{0.9}Si_{1.1}O_4$) Na-Al Carnegieite ($Na_{1.55}Al_{1.55}Si_{0.45}O_4$)	Quartz (SiO_2)
Z4	Troy	BB	725	K rich Nepheline ($K_{0.25}Na_{0.75}AlSiO_4$) Na-Al Carnegieite ($Na_{1.55}Al_{1.55}Si_{0.45}O_4$) Na_2CO_3 (Thermonatrite) Nitrited cancrinite ($Na_8[AlSiO_4]_6(OH)(NO_2) \bullet H_2O$)	Magnetite (Fe_3O_4) Anatase (TiO_2) Quartz (SiO_2)
Z1-48 hour	Sagger	BB	725	Na rich Nepheline ($Na_{0.83}Al_{0.78}Si_{1.22}O_4$) Sodalite ($Na_8Al_6Si_6O_{24}Cl_2$) – possibly nosean if SO_4 substituted for Cl_2 Combeite ($Na_{5.27}Ca_3Si_6O_{18}$)	Al_2O_3

Figure 9. Ternary phase diagram for the Na$_2$O-Al$_2$O$_3$-SiO$_2$ diagram with the composition of all of the BSR SBW campaigns shown.
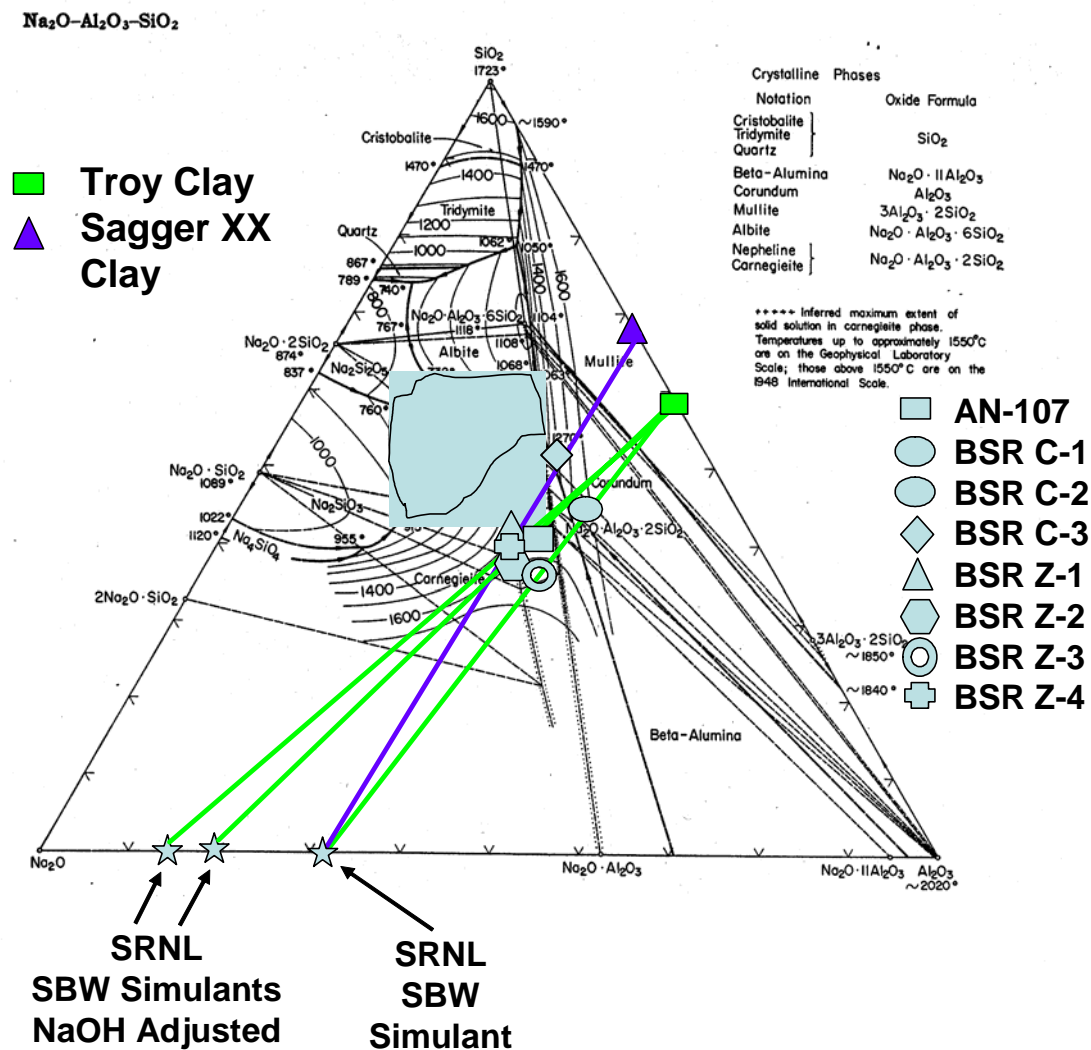
5.1.2 Hanford LAW Solid Phase Products

All of the BSR Hanford Steam Reformed products had a dark gray interior with a grayish-white exterior. The gray color was due to unreacted carbon in the product during the normal 4 hour residence time in the BSR. However, the H1 product that had a 48 hour residence time in the BSR had a white exterior color, but still had a gray interior as shown in Figure 10. Some of the H1 product was further baked in a regular furnace for three hours and it turned white throughout which indicates all the carbon was consumed. Since the BSR runs in an oxygen free environment, this indicates that oxygen was needed for complete carbon consumption. The form of all of the BSR Hanford products was the same as shown in Figure 10. For all the campaigns the waste loading was kept at a constant 23 wt%.

Figure 10. H1-48hr Steam Reformed Product

An approximately 3 inch piece of the H1-48hr product was baked in an oven at 650°C for three hours. Following heat treatment, the product was white throughout showing that all the carbon was baked out (in the presence of heat and oxygen).

The x-ray diffraction (XRD) results of the product phases produced are given in

Table 14. The cage structured nosean (SO_4 host phase) was observed in all of the 4-hour BSR products and in the H1-48 hour products. Nepheline was observed in all of the 4-hour BSR products (either stoichiometric nepheline, Na-rich nepheline or K-substituted nepheline along with metastable stoichiometric carnegieite or Na-rich carnegieite). In the H1-48 hour campaign, nosean and two nephelines were observed, e.g. the stoichiometric nepheline and a Na-rich nepheline and no metastable carnegieite was observed. These are the same two nepheline phases and the nosean phase that formed in the AN-107 pilot scale campaigns performed by TTT in a pilot scale demonstration at Hazen in Golden, Colorado. This again indicates that residence times in excess of 4 hours are needed in the BSR, e.g. the residence time needs to be optimized to match the phases produced in larger pilot scale facilities.

The LAW campaigns H1, H2, H4, and H6 used OptiKasT kaolin clay and the same clay/simulant ratio. Different temperatures, different carbons, and tests with and without the catalyst were used in the various campaigns. As with the SBW campaigns, the GC carbon did not perform as well as the BB carbon leaving both a large quantity of carbon residue in the product and unreacted $NaNO_3$ in campaigns H2 and H4 even at 3.2X the stoichiometric amount of carbon to nitrate/nitrite. For campaigns H1, H2, H4 and H6 the same major phases were found: nosean, nepheline and carnegieite. Campaign H1 had no minor phases present (Table 14). Campaign H2 had unreacted $NaNO_3$, muscovite mica which is an impurity in the OptiKasT clay [24], and amorphous carbon from the GC carbon which is not shown in Table 14. In campaign H4 at a lower REDOX stoichiometry of 1.6, Na_2CO_3 formed from the CO_2 produced as a minor phase. This phase did not appear in the H1, H2 and H6 campaigns that used the higher REDOX stoichiometry of 3.2 irregardless of the presence or absence of the catalyst. Campaigns H1, H2, H4 and H6 were compositionally very close to the AN-107 Hazen run in terms of their chemistry in the $(Na,K)_2O$-Al_2O_3-SiO_2 oxide system (Figure 11).

The LAW campaigns H3 and H5 used Sagger Clay at two different temperatures and two different REDOX ratios. Campaign H3 used a catalyst and H5 did not. Campaign H3 used GC carbon and campaign H5 used BB carbon. As with the SBW campaigns and the H2 campaign, the GC carbon left residual untreated $NaNO_3$. The H3 and H5 campaigns had the same major phases: nosean, nepheline and carnegieite (Table 14). Both campaigns had impurities from the Sagger clay, namely muscovite mica, quartz (SiO_2) and TiO_2. Interestingly, these campaigns were almost in the low melting nepheline region of the $(Na,K)_2O$-Al_2O_3-SiO_2 oxide system shaded in Figure 11. No evidence of partial melting of any of the starting materials or the products was observed.

LAW campaigns H7 and H8 used Troy Clay at two different temperatures and two different REDOX ratios. Campaign H8 used a catalyst and H7 did not. Campaign H7 used GC carbon and campaign H8 used BB carbon. Both campaigns produced Na_2CO_3 as a minor phase. The H7 campaign, reacted at the higher temperature, contained only nosean and nepheline. The H8 campaign contained nosean, nepheline, and carnegieite (Table 14). These differences indicate that higher temperatures encourage the stable nepheline to form over the metastable carnegieite. Both campaigns had impurities from the Troy clay, namely quartz (SiO_2) and TiO_2. The H7 and H8 campaigns were in the approximate region of the AN-107 Hazen testing and similar to the H1, H2, H4, and H6 campaigns shown on the $(Na,K)_2O$-Al_2O_3-SiO_2 oxide system shaded in Figure 11. However, the Troy clay

compositions were in a location closer to the nepheline phase region and the phases observed in the H7 test are likely a result of this more favorable chemistry.

Table 14. Solid Phases Identified in LAW BSR Campaigns by X-Ray Diffraction (XRD) Without Roasting

Sample ID	Type of Clay	Type of Carbon	Temp ^{o}C	Major Phases	Minor Phases
H1	OptiKasT	BB	725	nosean ($Na_8Al_6Si_6O_{24}SO_4$) nepheline ($NaAlSiO_4$) carnegieite ($NaAlSiO_4$)	None
H2	OptiKasT	GC	650	nosean ($Na_8Al_6Si_6O_{24}SO_4$) nepheline ($NaAlSiO_4$) carnegieite ($NaAlSiO_4$)	$NaNO_3$ Muscovite mica amorphous carbon
H3	Sagger	GC	725	nosean ($Na_8Al_6Si_6O_{24}SO_4$) Na rich Nepheline ($K_{0.12}Na_{0.87}Al_{0.99}Si_{1.01}O_4$) carnegieite ($NaAlSiO_4$)	$NaNO_3$ Muscovite mica Faujasite ($Na_{1.88}Al_2Si_{4.8}O_{13.54}$)
H4	OptiKasT	GC	725	nosean ($Na_8Al_6Si_6O_{24}SO_4$) Na rich Nepheline ($K_{0.12}Na_{0.87}Al_{0.99}Si_{1.01}O_4$) carnegieite ($NaAlSiO_4$)	Na_2CO_3
H5	Sagger	BB	650	nosean ($Na_8Al_6Si_6O_{24}SO_4$) Na rich Nepheline ($K_{0.12}Na_{0.87}Al_{0.99}Si_{1.01}O_4$) Na-Al Carnegieite ($Na_{1.55}Al_{1.55}Si_{0.45}O_4$)	Rutile/anatase (TiO_2) Quartz (SiO_2) Muscovite mica
H6	OptiKasT	BB	650	nosean ($Na_8Al_6Si_6O_{24}SO_4$) nepheline ($Na_{0.75}K_{0.25}Al_{0.88}Si_{1.12}O_4$) carnegieite ($NaAlSiO_4$)	Anatase (TiO_2)
H7	Troy	GC	725	nosean ($Na_8Al_6Si_6O_{24}SO_4$) nepheline ($Na_{0.75}K_{0.25}Al_{0.894}Si_{1.106}O_4$)	Anatase (TiO_2) Quartz (SiO_2) Na_2CO_3
H8	Troy	BB	650	nosean ($Na_8Al_6Si_6O_{24}SO_4$) nepheline ($Na_{0.75}K_{0.25}Al_{0.894}Si_{1.106}O_4$) carnegieite ($NaAlSiO_4$)	Quartz (SiO_2) Na_2CO_3
H1-48 hour	Sagger	BB	725	nosean ($Na_8Al_6Si_6O_{24}SO_4$) Na rich Nepheline ($Na_{0.89}Al_{0.9}Si_{1.1}O_4$) nepheline ($NaAlSiO_4$)	Cristobalite (SiO_2)

Figure 11. Ternary phase diagram for the Na_2O-Al_2O_3-SiO_2 diagram with the composition of all of the BSR LAW campaigns shown.
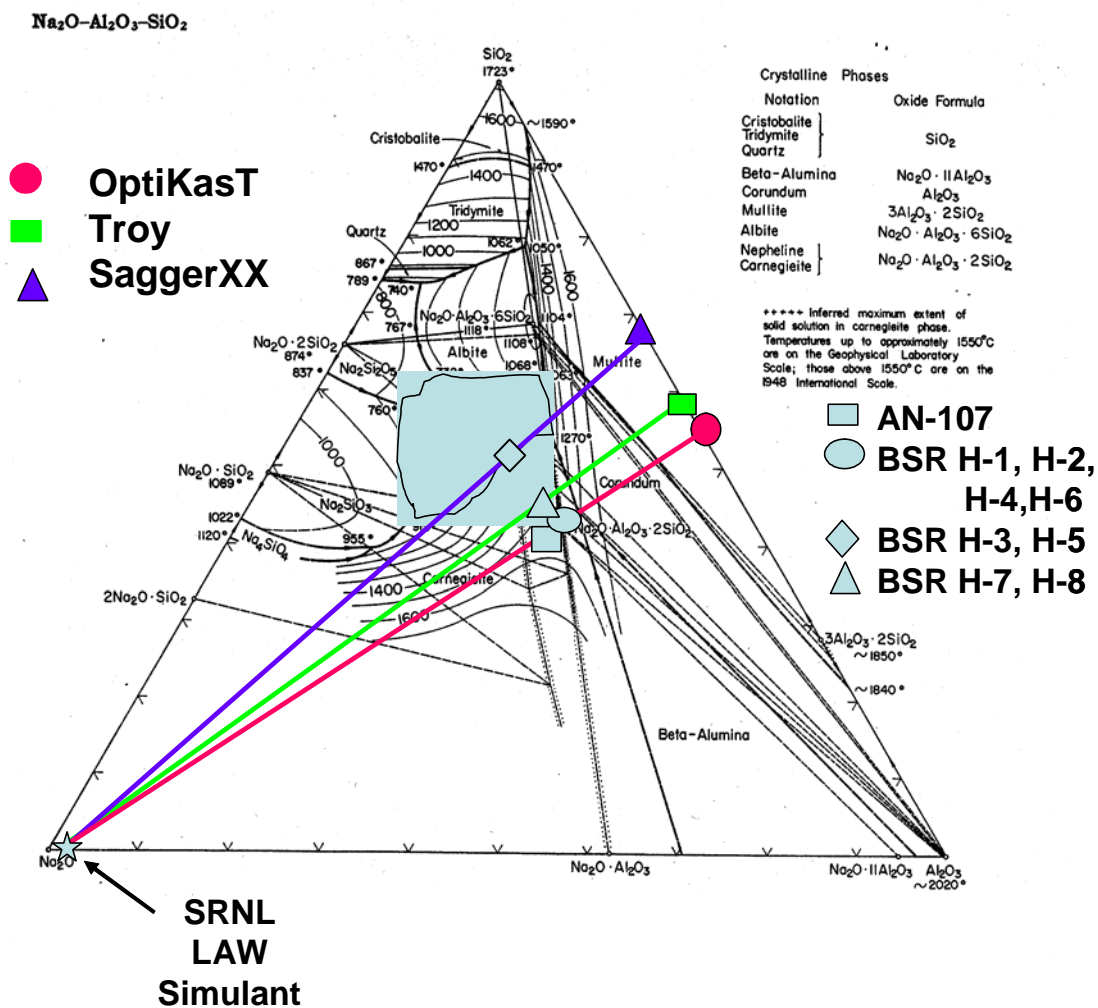
5.1.3 Target Vs. Measured Product Compositions

Selected samples (H-1, Z-1, Z-3 and Z-4) were analyzed by dissolution and Inductively Coupled Plasma Emission Spectroscopy (ICP-ES) for the major cations. The measurements were compared to the target values calculated using the MINCALC #3 spreadsheet for verification that the targets were calculated accurately. The target vs. measured major oxides on a calcined basis are given in Table 15. The target vs. measured major oxides are very similar. The Al_2O_3 concentrations of the measured samples is about 1-1.5 wt% high in all cases due to Al_2O_3 from the starting bed that became embedded in the BSR product during processing. The measured silica values appeared a little low indicating that free silica in the clay did not react to form mineralized product.

Table 15. Target values calculated using MINCALC#3 and measured major oxide in the BSR product phases on a calcined basis.

		SiO_2	ALKALI*	Al_2O_3
H-1	MINCALC#3	42.3	22.7	35.0
	Measured	40.2	22.2	37.6
Z-1	MINCALC#3	42.9	25.8	31.3
	Measured	40.4	26.7	32.9
Z-3	MINCALC#3	36.7	26.0	37.3
	Measured	34.8	26.8	38.4
Z-4	MINCALC#3	39.6	27.5	32.9
	Measured	38.1	27.7	34.1

* ALKALI = $Na_2O + K_2O + Cs_2O$

5.1.4 Product Comparison of BSR to Hazen and STAR FBSRs

Table 16 shows the comparison of the FBSR pilot scale products to the BSR products for comparable run conditions. The BSR sample H1 was comparable to the test conditions of the STAR facility campaign for the Hanford LAW simulant. The BSR sample Z1 was comparable to the test conditions of the STAR facility campaign for the INEEL SBW simulant. For both the H1 and the Z1 BSR campaigns a catalyst was used but no catalyst was used in the STAR facility campaigns. This did not alter the phases produced but altered the off-gas destruction. In addition, some oxygen was bled into the STAR facility campaigns but the BSR does not currently have the capability to bleed in oxygen. Again, this would alter the off-gas results but not the product phase development. The BSR sample AN-107 was comparable to the test conditions of the Hazen Research pilot campaigns. Both the Hazen Research campaigns and the BSR AN-107 campaign used the same catalyst.

The phase analyses given in Table 16 demonstrated that the shorter BSR campaigns tended to produce the metastable nepheline known as carnegieite but that the same feed compositions produced the stable nepheline phase when left for ~48 hours. The longer residence times are more representative of the bed residence times in the pilot scale facilities.

Table 16 demonstrates that both the 48 hour Z1 (SBW) campaigns made the same products phases as produced in the INEEL STAR facility, e.g. a K-Na bearing nepheline and a NaCl-Na_2SO_4-Na_2ReO_4 host phase (sodalite). The shorter BSR run (4 hours) produced the metastable Si-deficient carnegieite indicating incomplete reaction. The INEEL STAR campaign also indicated some incomplete reaction as excess $NaAl_{11}O_{17}$ and excess Al_2O_3 and SiO_2 were all produced, albeit in minor quantities. This indicates that improvements could be made in the particle size growth and reaction in the INEEL STAR pilot facility.

Table 16 demonstrates that both the 48 hour H1 (LAW) campaigns made the same products phases as produced in the INEEL STAR facility, e.g. two different types of nepheline and the Na_2SO_4-Na_2ReO_4 host phase (nosean). The shorter BSR run (4 hours) produced the metastable carnegieite of nominal composition indicating incomplete reaction. The INEEL STAR campaign also indicated some incomplete reaction as nominal carnegieite was found as a major phase. This also indicates that improvements could be made in the particle size growth and reaction in the INEEL STAR pilot facility.

Table 16 demonstrates that both the 16 hour AN-107 (LAW) campaign had insufficient reaction time (only 16 hours instead of 48) and some metastable carnegieite was made in addition to the desired stable nepheline and nosean (Na_2SO_4-Na_2ReO_4 host) phases. The same stable products phases (nepheline and nosean) were found in the Hazen Research pilot scale campaigns. This indicates that the BSR should be operated for ≥ 48 hours in order to reproduce the product phases and residence times of the FBSR pilot scale facilities.

Table 16. Product Comparison of BSR to Hazen and STAR Facilities

Sample ID	Residence Time (hrs)	Type of Clay/Catalyst	Type of Carbon	Temp (^{o}C)	Major Phases	Minor/Trace Phases
SODIUM BEARING WASTE DEMONSTRATIONS						
BSR - Z1	4 hrs	Sagger/Catalyst	BB	725	K rich Nepheline ($K_{0.12}Na_{0.87}Al_{0.99}Si_{1.01}O_4$) Na-Al Carnegieite, $Na_{1.55}Al_{1.55}Si_{0.45}O_4$	None
BSR Z1-48	48 hours	Sagger/ Catalyst	BB	725	Na rich Nepheline ($Na_{0.83}Al_{0.78}Si_{1.22}O_4$) Sodalite ($Na_8Al_6Si_6O_{24}Cl_2$)	Al_2O_3 Combeite ($Na_{5.27}Ca_3Si_6O_{18}$)
INEEL/STAR Bed 1173 COT 100	≥48 hours	Sagger/None	BB	725	K rich Nepheline ($K_{0.25}Na_{0.75}AlSiO_4$) Sodalite ($Na_8Al_6Si_6O_{24}Cl_2$)	Al_2O_3 and SiO_2 Combeite ($Na_{5.27}Ca_3Si_6O_{18}$) Beta-Alumina ($NaAl_{11}O_{17}$)
HANFORD LAW WASTE DEMONSTRATIONS						
BSR-H1	4 hrs	OptiKasT/ Catalyst	BB	725	Carnegieite ($NaAlSiO_4$) Nepheline ($NaAlSiO_4$) Nosean ($Na_8Al_6Si_6O_{24}SO_4$)	None
BSR-H1-48	48 hours	OptiKasT/ Catalyst	BB	725	Nepheline ($NaAlSiO_4$) Nosean ($Na_8Al_6Si_6O_{24}SO_4$) Na rich Nepheline ($Na_{0.89}Al_{0.9}Si_{1.1}O_4$)	SiO_2
INEEL/STAR Bed 1104 COT 55:30	≥48 hours	OptiKasT/None	BB	725	Carnegieite ($NaAlSiO_4$) Nosean ($Na_8Al_6Si_6O_{24}SO_4$) Na rich Nepheline ($Na_{0.89}Al_{0.9}Si_{1.1}O_4$)	TiO_2 (clay impurity)
HANFORD LAW WASTE DEMONSTRATIONS						
BSR-AN-107	16 hours	SnoBrite/Catalyst	BB	725	Na rich Nepheline ($Na_{0.83}Al_{0.78}Si_{1.22}O_4$) Carnegeite ($NaAlSiO_4$) Nosean ($Na_8Al_6Si_6O_{24}SO_4$)	Fe_2O_3 (catalyst) SiO_2
HAZEN RESEARCH	≥48 hours	SnoBrite/Catalyst	BB	725	Nepheline $NaAlSiO_4$ Nosean ($Na_8Al_6Si_6O_{24}SO_4$)	Al_2O_3 Fe_2O_3 (catalyst) Fe_3O_4 (catalyst)

5.2 GAS PHASE PRODUCTS

Four observations were made for the gas phase products of all campaigns: 1) the presence of any gas odor was noted, 2) the volume was determined, 3) the color was observed, and 4) a sample was run through a gas chromatograph. A distinct odor that was likened to perm solution for hair was in the offgas of all campaigns. This probably indicates the presence of ammonia, some organics, and possibly some sulfur were present. The volume of the gas based on the process conditions is shown in Table 17.

Table 17. Gas Volumes versus Process Conditions

Run	Temp	Redox	Catalyst	Carbon	Clay	ml gas/ g feed
C1	725	3.2	yes	BB	Troy	202.4
C2	650	3.2	yes	GC	Troy	122.4
C3	725	3.2	yes	GC	Sagger	127.7
Z3	725	2	yes	BB	Troy	352.6
Z4	725	2	yes	BB	Troy	300.8
H1	725	3.2	yes	BB	OptiKast	136.1
H2	650	3.2	yes	GC	OptiKast	76.69
H3	725	3.2	yes	GC	Sagger	70.09
H4	725	1.6	yes	GC	OptiKast	44.9
H5	650	1.6	no	BB	Sagger	46.7
H6	650	3.2	no	BB	OptiKast	74.0
H7	725	3.2	no	GC	Troy	117.4
H8	650	1.6	yes	BB	Troy	40.2
HB	725	0	no	none	OptiKast	

5.2.1 NOx Destruction Based on Gas Color for Hanford LAW Campaigns

The color of the offgas gives an indication of the extent of NO_x destruction. It is described by Beer's Law of light absorbance by a chemical compound.

Carbon is used in the steam reforming process to reduce NO_x gases to N_2 and CO. The CO can be oxidized in a further processing step to CO_2. The NO_x gases have a distinct color based on concentration that is easily distinguished by the unassisted eye. For each Hanford run a sample of the gas was introduced into a glass tube for color comparison with an appropriate paint color chart.

The glass tube gas color chamber had a 52mm ID and 55mm OD. Its volume, including all fittings was 416 ml as measured by filling it with water and getting a weight difference. Once the chamber was filled with gas, it was placed on the inside cover of a white notebook and the color was compared to appropriate paint color charts. The gas color chamber is shown in Figure 12.

Figure 12. Gas Color Chamber
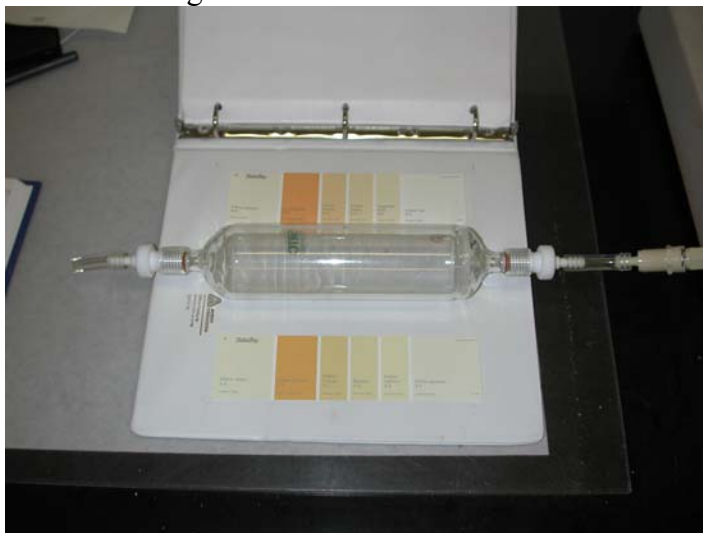
The colors from the paint color charts used were then compared to a computer screen color in Microsoft Word using the format: borders and shading: shading command. The colors were matched and the Red, Green, Blue (RGB) intensities were recorded. The intensities were then summed to give the total intensity. The % intensity is based on the darkest color being 0% and clear being 100%. The results of this exercise are shown in Table 18.

Table 18. Relative Color Chart

Color	RGB Intensity	Total Intensity	% Intensity
clear	255,255,255	765	100
7f-light	254,234,202	691	78
9f	255,221,153	629	60
8e	255,209,117	581	46
9d	254,204,104	562	41
9c	255,199,87	541	35
7b	255,141,27	423	0

A second baseline steam reforming run was performed on Hanford LAW and Optikast clay, but included no carbon or catalyst. This run produced the greatest concentration of NO_x gas which was then diluted and measured for color.

A gas mixture was obtained by putting the color tube under vacuum, then injecting a measured amount of baseline run gas, then relieving the vacuum by allowing air to be sucked into the chamber. The color would then be observed and recorded and the tube would be cleared by having air blown through it before the next mixture was introduced. This was done for as many concentrations as we could discern a color difference. The color was then put into a table as a %intensity based on Table 18. The %intensity is assumed equal to the %transmittance in Beer's Law. The absorbance was then calculated from the %transmittance by:

Absorbance = $2 - \log_{10}$ (%Transmittance).

The concentration of the baseline gas in the color tube was the number of milliliters of gas injected divided by the total volume of 416 milliliters. The %NO_x destruction was calculated as:

%NO_x destruction = 100 x (1-NO_x Concentration).

The data from the color mixtures are shown in Table 19.

Table 19. Color Mixture Data and %NO_x Destruction for Hanford Campaigns

ml gas	Conc.	%xmittance	absorbance	% destruction
0	0.0000	100	0.0000	100
10	0.0240	100	0.0000	98
15	0.0361	60	0.2218	96
20	0.0481	60	0.2218	95
30	0.0721	46	0.3372	93
40	0.0962	43	0.3665	90
50	0.1202	41	0.3872	88
60	0.1442	35	0.4559	86
70	0.1683	25	0.6021	83
80	0.1923	20	0.6990	81
90	0.2163	15	0.8239	78
100	0.2404	10	1.0000	76
176	0.4231	5	1.3010	58
234	0.5625	1	2.0000	44
416	1.0000	1	2.0000	0

Absorbance can then be plotted against the %NO_x destruction for a straight line graph. The coefficient of determination (R^2) of .98 is close to 1 and indicates a good fit to the line. The plot is shown in Figure 13.

Figure 13. %NO$_x$ Destruction versus Absorbance for Hanford Campaigns
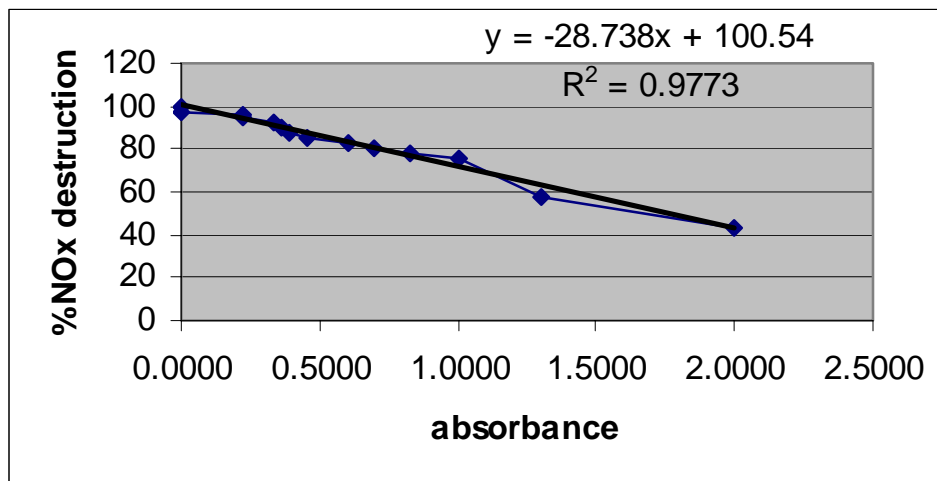
The %NOx destruction numbers from the color chart can now be applied to the Hanford gas samples as is shown in Table 20.

Table 20. NOx Destruction for Hanford Campaigns

Run	Temp	Redox	Catalyst	Carbon	Clay	Color, %NO$_x$ Destroyed
H1	725	3.2	yes	BB	OptiKast	95
H2	650	3.2	yes	GC	OptiKast	86
H3	725	3.2	yes	GC	Sagger	93
H4	725	1.6	yes	GC	OptiKast	86
H5	650	1.6	no	BB	Sagger	>98
H6	650	3.2	no	BB	OptiKast	>98
H7	725	3.2	no	GC	Troy	95
H8	650	1.6	yes	BB	Troy	88
HB	725	0	no	none	OptiKast	0

Statistics were applied to the eight run matrix to determine the best combination of process conditions for the destruction of offgas NO$_x$. The best conditions for NO$_x$ destruction are to use the BB carbon and no catalyst. Catalyst did not aid in the reduction of NO$_x$ gas generated, but it may aid in the destruction of NO$_3$ from the feed. Clay type, REDOX, and temperature had little effect on NO$_x$ destruction. Of particular interest from these analyses was the REDOX finding. This showed that a level of 1.6 stoichiometric carbon addition was adequate to facilitate offgas NO$_x$ destruction. The statistics are shown in appendix B.

The NO$_x$ destruction for the INEEL campaigns was not determined (since a "no carbon" run was not performed). However, the gas color for the INEEL campaigns is shown in Table 17 for a qualitative comparison.

5.2.2 Gas Chromatography of Offgases

The gas chromatograph (GC) was used to measure the volume percent of hydrogen, oxygen, nitrogen, carbon monoxide, and carbon dioxide in the noncondensable offgas downstream of the moisture condenser and desiccant. Table 21 lists the gas chromatograph output. The gas compositions indicate more reducing gas conditions from the BSR tests than have been observed in the INEEL pilot-scale tests, with higher H_2 and CO contents, and a higher proportion of CO compared to CO_2. The STAR pilot-scale FBSR has oxygen bled into the fluidized bed and measures the gas concentrations after an oxidizer which does not exist on the BSR.

Table 21. Gas Chromatograph Results for Gases, Dry Basis

Run	Temp	REDOX	Catalyst	Clay	Carbon	H_2	O_2	N_2	CO	CO_2
						vol%	vol%	vol%	vol%	vol%
C1	725	3.2	yes	Troy	BB	41	1	19	8.8	2
C2	650	3.2	yes	Troy	GC	16	0	28	9.5	1.7
C3	725	3.2	yes	Sagger	GC	32	0.25	18	16	1.1
Z3	725	2	yes	Troy	BB	54	0.38	22	3.3	0.32
Z4	725	2	yes	Troy	BB	56	0.18	5.2	4.6	0.44
H1	725	3.2	y	Optikast	BB	49	0.45	10	3	0.9
H2	650	3.2	y	Optikast	GC	82	0	14	2.6	0.52
H3	725	3.2	y	Sagger	GC	36	0.8	17	6	0.6
H4	725	1.6	y	Optikast	GC	65	0	18	3.6	0.48
H5	650	1.6	n	Sagger	BB	35	0	19	4.2	0.77
H6	650	3.2	n	Optikast	BB	40	0	12	2.4	0.66
H7	725	3.2	n	Troy	GC	50	0	8	2.6	0.36
H8	650	1.6	y	Troy	BB	21	0	20	0.77	0.55
HB	725	0	n	Optikast	none	3	0	32	0.72	0.32

The amount of feed was used to calculate the amount of each gas species produced per gram of feed. Table 22 shows the gas species production on a per gram feed basis.

Table 22. Gas Species Production per Gram Slurry Feed

Run	Temp	Redox	Clay	Carbon	ml H_2/ g feed	ml O_2/ g feed	ml N_2/ g feed	ml CO/ g feed	ml CO_2/ g feed	ml gas/ g feed
C1	725	3.2	Troy	BB	82.98	2.02	38.45	17.81	4.05	202.4
C2	650	3.2	Troy	GC	19.58	0.00	34.27	11.63	2.08	122.4
C3	725	3.2	Sagger	GC	40.86	0.32	22.98	20.43	1.40	127.7
Z3	725	2	Troy	BB	190.41	1.34	77.57	11.64	1.13	352.6
Z4	725	2	Troy	BB	168.48	0.54	15.64	13.84	1.32	300.8
H1	725	3.2	Optikast	BB	66.64	0.61	13.60	4.08	1.22	136.1
H2	650	3.2	Optikast	GC	62.83	0.00	10.73	1.99	0.40	76.69
H3	725	3.2	Sagger	GC	25.48	0.57	12.03	4.25	0.42	70.09
H4	725	1.6	Optikast	GC	29.17	0.00	8.08	1.62	0.22	44.9
H5	650	1.6	Sagger	BB	16.32	0.00	8.86	1.96	0.36	46.7
H6	650	3.2	Optikast	BB	29.59	0.00	8.88	1.78	0.49	74
H7	725	3.2	Troy	GC	58.72	0.00	9.40	3.05	0.42	117.4
H8	650	1.6	Troy	BB	8.44	0.00	8.04	0.31	0.22	40.2

6.0 CONCLUSIONS

6.1 USE OF BSR FOR EVALUATING STEAM REFORMER TECHNOLOGY

The BSR proved to be an effective tool to evaluate treatment of wastes by the FBSR technology. The product results obtained in the BSR were consistent with those obtained in the STAR facility pilot-scale system and the TTT pilot scale runs at Hazen [3]. Additionally, NO_x destruction readily occurred in the BSR and a simple colorimetric system was derived to determine NO_x destruction. The BSR proved to be a useful tool for determining appropriate conditions for larger scale FBSR operations.

6.2 CONCLUSIONS FOR INEEL SBW SIMULANT

- For the INEEL SBW, the BSR Z1 campaign with Sagger clay produced the desired nepheline phase and some metastable carnegieite during a normal 4 hour campaign; no minor or unreacted phases were observed in the final mineral products.

  - These are the same phases observed in the INEEL pilot scale tests at the STAR facility

- For the INEEL SBW, the BSR Z1 campaign with Sagger clay produced the desired nepheline and sodalite phases during a 48 hour campaign, which indicates that the longer residence times (>4 hours) are needed in the BSR to stabilize nepheline and sodalite over carnegieite, e.g. the presence of metastable carnegieite indicates that all of the reactions are not complete and the residence time is too short

- For the INEEL SBW, the BSR campaigns with Troy clay and excess NaOH produced the desired phases during 4 hour campaigns indicating that processing on the caustic side appeared to increase reactivity and mineral formation. However, excess NaOH caused an interaction between the NaOH and the CO_2 being evolved forming Na_2CO_3; this may also be caused by the REDOX stoichiometry being too low (2X vs. 3.2X) and/or the residence time being too short (only 4 hours)

- Using BB carbon with catalyst produced >98% offgas NO_x destruction. However, based on tests performed with the Hanford simulant, the same NO_x destruction could probably be attained using BB carbon with no catalyst. Offgas NO_x destruction is defined as the reduction of gaseous NO_x to N_2 and is not the % destruction of NO_x in the feed solution.

6.3 CONCLUSIONS FOR HANFORD LAW SIMULANT

- For the Hanford Low Activity Waste (LAW) the BSR campaigns produced the desired nosean (SO_4 host) and nepheline phases and some metastable carnegieite in essentially all of the normal 4 hour campaigns; no minor or unreacted phases were observed in the final mineral products. Campaign H7 did not produce the metastable carnegieite.

  ➢ These were the same phases observed during pilot scale testing of the AN-107 by THOR[sm].

- In the H1-48 hour campaign, nosean and two nephelines were observed, e.g., the stoichiometric nepheline and a Na-rich nepheline and no metastable carnegieite was observed.

- The H7 campaign, reacted at the higher temperature, contained only nosean and nepheline. The H7 composition was in a location closer to the nepheline phase region and the phases observed in the H7 test are likely a result of this more favorable chemistry.

- The GC carbon was found to be inferior to the BB carbon and left both a carbon residue and unreacted $NaNO_3$: in some cases GC carbon preferentially stabilized Na_2CO_3 over the desired nosean/nepheline sodium aluminosilicate minerals.

- The MINCALC#3 spreadsheet used to target the BSR campaigns was verified by analyzing the H1, Z1, Z3 and Z4 products: the target and analyzed compositions matched within 1-1.5 wt% on an oxide basis.

- Statistics were applied to the eight run matrix to determine the best combination of process conditions for the destruction of offgas NO_x. Using BB carbon with no catalyst produced >98% destruction of the offgas NO_x produced which is optimum. (Note that for these experiments, no oxygen was bled into the BSR which may affect catalyst effectiveness.)

- The two temperatures of 650^oC and 725^oC had no appreciable effect on offgas NO_x destruction.

- Neither the type of clay nor the REDOXs of 1.6 versus 3.2 had an effect on the offgas NO_x destruction.

7.0 ACKNOWLEDGEMENTS

8.0 FUTURE WORK

Based on the work performed using the BSR and the comments received for this report, the following recommendations for future work are:

- Analyze mineral product for nitrates to determine percent nitrate destruction from the feed.

- Further explore the effect of residence time on mineral formation.

- Determine mass of residual carbon in mineral product and relate this to NO_x destruction in the gas phase.

- Add oxygen to the offgas sample, after sampling for GC analysis, to convert all NO to NO_2 to get a better NO_2 color reading. Analyze and quantify condenser condensate for nitrates.

APPENDIX A. MINCALC 3 SPREADSHEET (PARTIAL)

	A	B	C	D	E	F	G	H	I	J	K	L
1	BATCHING SHEET (June 2004)				MINCALC #3 - H1 and H6 LAW DEMO WITH OPTIKAST CLAY							
2	MASS BALANCE FBSR-JANTZEN, MARRA, AND MASON											
3		ENTER			ENTER			Elem.				
4		Waste	Wet	Wet	Elem.			Calcine				
5		Comp		Elemental	Clay Comp	Oxide	Oxide	Clay + Waste				
6				Waste		Clay	Waste	Comp.		Grav.	Oxide	Norm. Oxide
7	Element	(M/L)	(gms/L)	(gms/100g)	(gms/100g)	Wt%	Wt%	gms/100g	Oxide	Factors	Wt	Wt%
8	Al	0.06987	1.89	#DIV/0!	22.70	42.89	#DIV/0!	#DIV/0!	Al2O3	1.8895	#DIV/0!	#DIV/0!
9	As			#DIV/0!		0.00	#DIV/0!	#DIV/0!	As2O3	1.3203	#DIV/0!	#DIV/0!
10	B		0.00	#DIV/0!		0.00	#DIV/0!	#DIV/0!	B2O3	3.2201	#DIV/0!	#DIV/0!
11	Ba			#DIV/0!		0.00	#DIV/0!	#DIV/0!	BaO	1.1165	#DIV/0!	#DIV/0!
12	Ca		0.00	#DIV/0!	0.02	0.03	#DIV/0!	#DIV/0!	CaO	1.3992	#DIV/0!	#DIV/0!
13	Cd			#DIV/0!		0.00	#DIV/0!	#DIV/0!	CdO	1.1423	#DIV/0!	#DIV/0!
14	Ce			#DIV/0!		0.00	#DIV/0!	#DIV/0!	Ce2O3	1.1713	#DIV/0!	#DIV/0!
15	Co			#DIV/0!		0.00	#DIV/0!	#DIV/0!	CoO	1.2714	#DIV/0!	#DIV/0!
16	Cr	0.01005	0.52	#DIV/0!		0.00	#DIV/0!	#DIV/0!	Cr2O3	1.4616	#DIV/0!	#DIV/0!
17	Cs	0.00000051	0.00	#DIV/0!		0.00	#DIV/0!	#DIV/0!	Cs2O	1.0602	#DIV/0!	#DIV/0!
18	Cu		0.00	#DIV/0!		0.00	#DIV/0!	#DIV/0!	Cu2O	1.1259	#DIV/0!	#DIV/0!
19				#DIV/0!		0.00	#DIV/0!	#DIV/0!	CuO	1.2518	#DIV/0!	#DIV/0!
20	Fe		0.00	#DIV/0!	0.26	0.37	#DIV/0!	#DIV/0!	Fe2O3	1.4297	#DIV/0!	#DIV/0!
21				#DIV/0!		0.00	#DIV/0!	#DIV/0!	FeO	1.2865	#DIV/0!	#DIV/0!
22	K	0.023632	0.92	#DIV/0!	0.12	0.15	#DIV/0!	#DIV/0!	K2O	1.2046	#DIV/0!	#DIV/0!
23	La			#DIV/0!		0.00	#DIV/0!	#DIV/0!	La2O3	1.1728	#DIV/0!	#DIV/0!
24	Li			#DIV/0!		0.00	#DIV/0!	#DIV/0!	Li2O	2.1525	#DIV/0!	#DIV/0!
25	Mg		0.00	#DIV/0!	0.01	0.02	#DIV/0!	#DIV/0!	MgO	1.6583	#DIV/0!	#DIV/0!
26	Mn		0.00	#DIV/0!		0.00	#DIV/0!	#DIV/0!	MnO	1.2912	#DIV/0!	#DIV/0!
27	Mo			#DIV/0!		0.00	#DIV/0!	#DIV/0!	MoO3	1.5003	#DIV/0!	#DIV/0!
28	Na	4.95652	114.00	#DIV/0!	0.02	0.03	#DIV/0!	#DIV/0!	Na2O	1.3480	#DIV/0!	#DIV/0!
29	Nd			#DIV/0!		0.00	#DIV/0!	#DIV/0!	Nd2O3	1.1660	#DIV/0!	#DIV/0!
30	Ni		0.00	#DIV/0!		0.00	#DIV/0!	#DIV/0!	NiO	1.2726	#DIV/0!	#DIV/0!
31	P	0.0492	1.52	#DIV/0!	0.02	0.05	#DIV/0!	#DIV/0!	P2O5	2.2910	#DIV/0!	#DIV/0!
32	Pb		0.00	#DIV/0!		0.00	#DIV/0!	#DIV/0!	PbO	1.0772	#DIV/0!	#DIV/0!
33	Pu			#DIV/0!		0.00	#DIV/0!	#DIV/0!	PuO2	1.1311	#DIV/0!	#DIV/0!
34	Rb			#DIV/0!		0.00	#DIV/0!	#DIV/0!	Rb2O	1.0936	#DIV/0!	#DIV/0!
35	Re	0.0003953	0.07	#DIV/0!		0.00	#DIV/0!	#DIV/0!	ReO2	1.1719	#DIV/0!	#DIV/0!
36	Ru			#DIV/0!		0.00	#DIV/0!	#DIV/0!	RuO2	1.3166	#DIV/0!	#DIV/0!
37	Sb			#DIV/0!		0.00	#DIV/0!	#DIV/0!	Sb2O3	1.1970	#DIV/0!	#DIV/0!
38	Se			#DIV/0!		0.00	#DIV/0!	#DIV/0!	SeO2	1.4052	#DIV/0!	#DIV/0!
39	Si			#DIV/0!	24.65	52.73	#DIV/0!	#DIV/0!	SiO2	2.1393	#DIV/0!	#DIV/0!
40	Sn			#DIV/0!		0.00	#DIV/0!	#DIV/0!	SnO2	1.2696	#DIV/0!	#DIV/0!
41	Sr			#DIV/0!		0.00	#DIV/0!	#DIV/0!	SrO	1.1826	#DIV/0!	#DIV/0!
42	Tc			#DIV/0!		0.00	#DIV/0!	#DIV/0!	TcO2	1.3265	#DIV/0!	#DIV/0!
43	Te			#DIV/0!		0.00	#DIV/0!	#DIV/0!	TeO2	1.2508	#DIV/0!	#DIV/0!
44	Th			#DIV/0!		0.00	#DIV/0!	#DIV/0!	ThO2	1.1379	#DIV/0!	#DIV/0!
45	Ti			#DIV/0!	1.06	1.77	#DIV/0!	#DIV/0!	TiO2	1.6680	#DIV/0!	#DIV/0!
46	U			#DIV/0!		0.00	#DIV/0!	#DIV/0!	U3O8	1.1792	#DIV/0!	#DIV/0!
47	Y			#DIV/0!		0.00	#DIV/0!	#DIV/0!	Y2O3	1.2699	#DIV/0!	#DIV/0!
48	Zn		0.00	#DIV/0!		0.00	#DIV/0!	#DIV/0!	ZnO	1.2447	#DIV/0!	#DIV/0!
49	Zr			#DIV/0!		0.00	#DIV/0!	#DIV/0!	ZrO2	1.3508	#DIV/0!	#DIV/0!
50	F (IC)	0.03042	0.58	#DIV/0!		0.00	#DIV/0!	#DIV/0!	NaF	2.2104	#DIV/0!	#DIV/0!
51	Cl (IC)	0.04443	1.58	#DIV/0!		0.00	#DIV/0!	#DIV/0!	NaCl	1.6485	#DIV/0!	#DIV/0!
52	I(IC)	0.0000113	0.00	#DIV/0!		0.00	#DIV/0!	#DIV/0!	NaI	1.1812	#DIV/0!	#DIV/0!
53	SO4 (IC)	0.09177	8.82	#DIV/0!					Na2SO4	1.4787	#DIV/0!	#DIV/0!
54	NO2 (IC)	0.412										
55	NO3 (IC)	2.5646										
56	SUMS	8.25	129.90	#DIV/0!	48.87	98.04	#DIV/0!	#DIV/0!			#DIV/0!	#DIV/0!
57												

	A	B	C		K	L
58	IDEAL ATOMIC RATIOS	ACTUAL	ACTUAL		CHECK TERNARY (OXIDE WT%)	
59	FOR NEPHELINE/SODALITE	From Elem	From Oxide			
60	M/Si = 1-1.33	#DIV/0!	#DIV/0!		SiO2	#DIV/0!
61	M/Al = 1-1.33	#DIV/0!	#DIV/0!		ALKALI	#DIV/0!
62	Al/Si ≥ 1	#DIV/0!	#DIV/0!		Al2O3	#DIV/0!
63	M/Al+Si = 0.5-0.67	#DIV/0!	#DIV/0!		SUM	#DIV/0!

	A	B	C	D	E	F
64	CHECK USAGE OXIDE MOLES (COL. O)			CHECK WT% PHASES		
65			OXIDES		MW of NAS	
66	K0.5Na1.5Al2Si2O8 (K-nepheline)	#DIV/0!	#DIV/0!	#DIV/0!	292.16	Balance off K
67	or K2Na6Al8Si8O32					
68	Na2Al2Si2O8 (nepheline)	#DIV/0!	#DIV/0!	#DIV/0!	284.11	Balance off Excess Na
69	Na8Al6Si6O24(SO4) (nosean)	#DIV/0!	#DIV/0!	#DIV/0!	994.37	Balance off SO4
70	Na8Al6Si6O24(F2) (sodalite)	#DIV/0!	#DIV/0!	#DIV/0!	936.31	Balance off F
71	Na8Al6Si6O24(Cl2) (sodalite)	#DIV/0!	#DIV/0!	#DIV/0!	969.21	Balance off Cl
72	Ex Al2O3	#DIV/0!	#DIV/0!	#DIV/0!		
73	Ex SiO2	#DIV/0!	#DIV/0!	#DIV/0!		
74	SUMS		#DIV/0!	#DIV/0!		
75	Ex Alk after B64, B65, B66 and B67	#DIV/0!		#DIV/0!		

APPENDIX B. STATISTICS FOR DETERMINING NO$_X$ DESTRUCTION

Response % Color Intensity
Actual by Predicted Plot

% Color Intensity Predicted P=0.0900
RSq=1.00 RMSE=3.4017
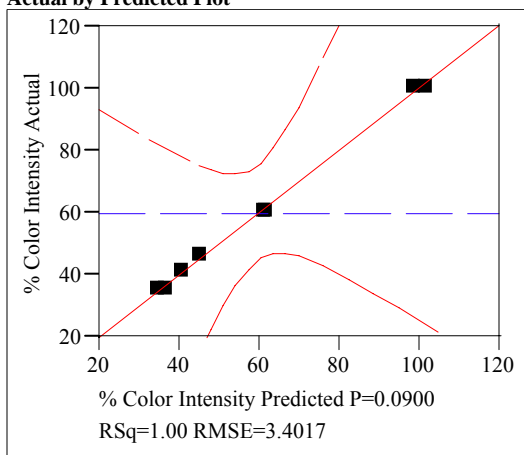
Summary of Fit

RSquare	0.997688
RSquare Adj	0.983819
Root Mean Square Error	3.40168
Mean of Response	59.625
Observations (or Sum Wgts)	8

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	6	4994.3036	832.384	71.9344
Error	1	11.5714	11.571	Prob > F
C. Total	7	5005.8750		0.0900

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	42.821429	25.80497	1.66	0.3453
Temp	0.0219048	0.038333	0.57	0.6695
REDOX	2.2321429	1.751343	1.27	0.4235
Catalyst[no]	19.214286	1.401075	13.71	0.0463
Carbon[BB]	11.678571	1.437472	8.12	0.0780
Clay[OptiKast]	2.9761905	1.767045	1.68	0.3411
Clay[Sagger]	9.7619048	1.91663	5.09	0.1234

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Temp	1	1	3.7786	0.3265	0.6695
REDOX	1	1	18.7970	1.6244	0.4235
Catalyst	1	1	2176.2707	188.0728	0.0463
Carbon	1	1	763.7786	66.0056	0.0780
Clay	2	2	539.0756	23.2934	0.1450

Correlation of Estimates

| Corr	Intercept	Temp	REDOX	Catalyst[no]	Carbon[BB]	Clay[OptiKast]	Clay[Sagger]
Intercept	1.0000	-0.984	0.0352	-0.155	-0.446	-0.064	0.0297
Temp	-0.984	1.0000	-0.205	0.2052	0.4000	0.1085	-0.05
REDOX	0.0352	-0.205	1.0000	-0.263	0.2052	-0.334	0.1539
Catalyst[no]	-0.155	0.2052	-0.263	1.0000	-0.205	0.3338	-0.154
Carbon[BB]	-0.446	0.4000	0.2052	-0.205	1.0000	-0.108	0.0500
Clay[OptiKast]	-0.064	0.1085	-0.334	0.3338	-0.108	1.0000	-0.461
Clay[Sagger]	0.0297	-0.05	0.1539	-0.154	0.0500	-0.461	1.0000

Appendix B, STATISTICS FOR DETERMINING NO$_X$ DESTRUCTION

Least Squares Fit
Response % Color Intensity
Whole Model
Actual by Predicted Plot

% Color Intensity Predicted P=0.0050
RSq=0.88 RMSE=10.965
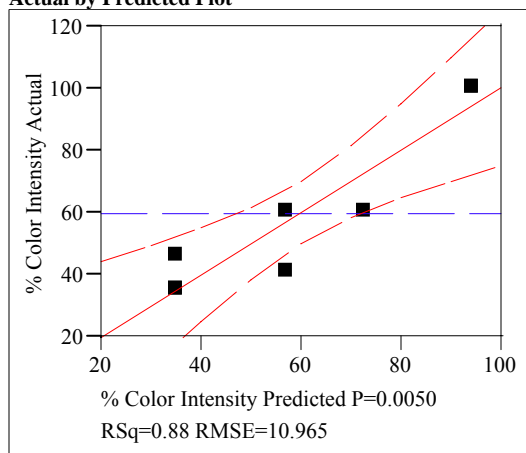
Summary of Fit

RSquare	0.879905
RSquare Adj	0.831868
Root Mean Square Error	10.9652
Mean of Response	59.625
Observations (or Sum Wgts)	8

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	2	4404.6964	2202.35	18.3169
Error	5	601.1786	120.24	Prob > F
C. Total	7	5005.8750		0.0050

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	1	340.01190	340.012	5.2076
Pure Error	4	261.16667	65.292	Prob > F
Total Error	5	601.17857		0.0846
				Max RSq
				0.9478

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	64.303571	4.012854	16.02	<.0001
Catalyst[no]	18.714286	4.144458	4.52	0.0063
Carbon[BB]	10.946429	4.012854	2.73	0.0414

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Catalyst	1	1	2451.5714	20.3897	0.0063
Carbon	1	1	894.6881	7.4411	0.0414

Appendix B, STATISTICS FOR DETERMINING NO$_X$ DESTRUCTION

Residual by Predicted Plot
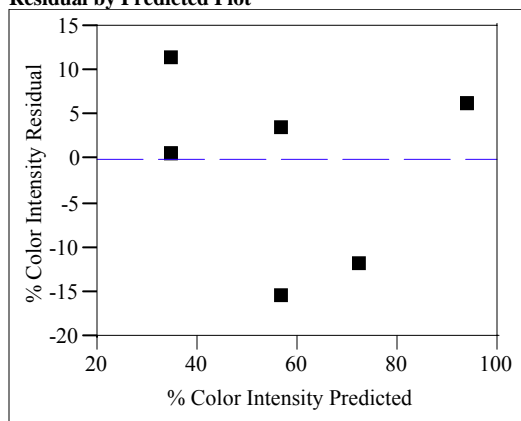
Catalyst
Leverage Plot
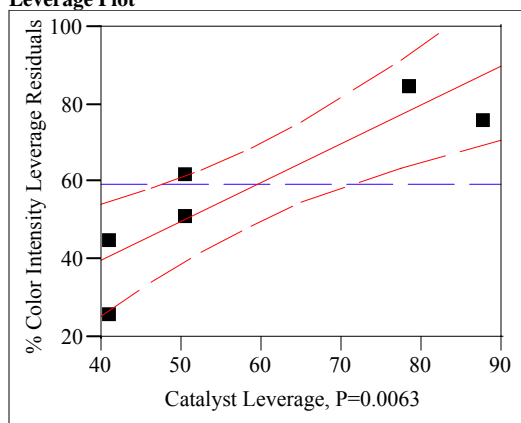
Least Squares Means Table

Level	Least Sq Mean	Std Error	Mean
no	83.017857	6.4705327	86.6667
yes	45.589286	4.9690304	43.4000

Carbon
Leverage Plot
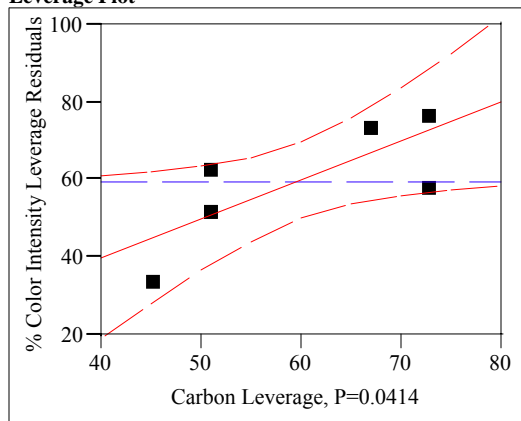
Least Squares Means Table

Level	Least Sq Mean	Std Error	Mean
BB	75.250000	5.4826024	75.2500
GC	53.357143	5.8611485	44.0000

51

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