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Saltstone Clean Cap Formulation

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Acronyms

ACTL	Aiken County Technical Laboratory
CCBT	Clean Cap Batch Tank
HRWR	High Range Water Reducer
N/M	Not Measured
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
SSHT	Salt Solution Hold Tank

Saltstone Clean Cap Formulation

1.0 SUMMARY

The current operation strategy for using Saltstone Vault 4 to receive 0.2 Ci/gallon salt solution waste involves pouring a clean grout layer over the radioactive grout prior to initiating pour into another cell. This will minimize the radiating surface area and reduce the dose rate at the vault and surrounding area. The Clean Cap will be used to shield about four feet of Saltstone poured into a Z-Area vault cell prior to moving to another cell. The minimum thickness of the Clean Cap layer will be determined by the cesium concentration and resulting dose levels and it is expected to be about one foot thick based on current calculations for 0.1 Ci Saltstone that is produced in the Saltstone process by stabilization of 0.2 Ci salt solution.

This report documents experiments performed to identify a formulation for the Clean Cap. Thermal transient calculations, adiabatic temperature rise measurements, pour height, time between pour calculations and shielding calculations were beyond the scope and time limitations of this study. However, data required for shielding calculations (composition and specific gravity) are provided for shielding calculations.

The approach used to design a Clean Cap formulation was to produce a slurry from the reference premix (10/45/45 weight percent cement/slag/fly ash) and domestic water that resembled as closely as possible the properties of the Saltstone slurry. In addition, options were investigated that may offer advantages such as less bleed water and less heat generation. The options with less bleed water required addition of dispersants. The options with lower heat contained more fly ash and less slag.

A mix containing 10/45/45 weight percent cement/slag/fly ash with a water to premix ratio of 0.60 is recommended for the Clean Cap. Although this mix may generate more than 3 volume percent standing water (bleed water), it has rheological, mixing and flow properties that are similar to previously processed Saltstone.

The recommended Clean Cap mix generates more bleed water than the reference Saltstone formulation because the specific gravity of water, the carrier fluid, is less than that of the carrier fluid in Saltstone, 1 versus 1.1 to 1.2, respectively. In addition, the development of slurry structure as a result of hydration reactions is slightly slower than in the salt solution slurry. In other words, the Clean Cap mix has a slightly longer gel time. The lower density of the carrier fluid and the slower development of slurry structure, enable more settling to occur (more standing water) in the Clean Cap slurry. Consequently, for the same rheological properties, the Clean Cap slurry will have more bleed water.

In an attempt to reduce the bleed water, the water to premix ratio was lowered and dispersants (high range water reducers) were added. Below water to premix ratios of 0.35, little bleed water and settling was observed. However, a low water to premix Clean Cap mix is not recommended because processing has not been demonstrated in the Saltstone facility. The lowest water to premix ratio processed in Z-Area was 0.478 in the last attempt to produce a clean cap. Although this option may provide significant advantages (less bleed water and potentially better flow) process testing in the Saltstone Facility or in a pilot scale facility in

conjunction with laboratory testing will be required to demonstrate mixing, pumping and flow properties.

Other additives were tested to minimize bleed water. These additives were found to be unsatisfactory in one or more ways and therefore, were not recommended at this time. An air entraining agent and a thickener had some benefit in reducing bleed water but were found too difficult to implement as an additive in the Saltstone facility. Surfactants (air entrainers) added to the mixing water in the hold tank could generate foam as the result of agitation to mix the tank, and the thickener increased the apparent viscosity and yield stress.

Low heat clean cap mixes in which all or some of the slag was replaced by fly ash in the premix formulation were also evaluated. The low heat mixes require less water than the reference clean cap mix. (Angular slag particles result in slurries with a higher water demand than do spherical fly ash particles.) Consequently more water (or salt solution) can be used if slag is incorporated in the premix before bleed water is generated. At water to premix ratios above 0.50, all of the low heat mixes generated more bleed water than the recommended mix. If processibility, pumpability and flow of grouts containing water to premix ratios below about 0.35 are demonstrated, the low heat mixes with less slag should be re-evaluated because they offer several advantages including lower cost and lower heat. However, at this time, such mixes can not be recommended due to lack of processing experience.

The recommended Clean Cap mix contains the reference Saltstone premix ingredients in the reference proportions. It has a compressive strength of greater than 200 psi after curing for 10 days but has between 3 and 6 volume percent bleed water depending on the shear conditions on the slurry. Different shear conditions were obtained in the laboratory by mixing (stirring) in a beaker versus mixing in a blender. Correlation of the laboratory results with the performance obtained during actual processing and placement (placement surface porosity, salt concentration, saturation, temperature, roughness, slope, etc.) is required to more accurately predict the volume of bleed water expected.

Site domestic water (chlorinated) was used in the admixture screening tests performed in N-Area. Another source of chlorinated domestic water (Talatha, Aiken County) was used to make the slurries for rheology flow curve determinations. (This water is maintained at 0.6 mg/L Cl.) No differences in slurry properties were apparent to visual observation. If water quality is identified as a problem in Z-Area and if the problem is limited to chlorine, concrete admixtures to regulate set are available and have been used in previous Saltstone processing. In the past, retarding admixtures were added to the make up water hold tank. If a deflocculated dilatant slurry is required (rather than the recommended Clean Cap slurry) to reduce bleed water, liquid high range water reducers can also be added to the makeup water hold tank. Consequently, a means of adding one or more liquid chemicals for modifying slurry properties should be addressed for the 0.2 Ci process.

2.0 INTRODUCTION

The current operation schedule for the Saltstone facility requires placement of a Clean Cap, non-radioactive grout, in the cells in Z-Area Vault 4 to provide shielding for Saltstone containing high cesium loadings [1]. The Clean Cap will be used to minimize "sky shine" by covering (shielding) about four feet of Saltstone poured into a Z-Area vault cell prior to moving to another cell. The minimum thickness of the Clean Cap layer will be determined by the cesium concentration and resulting dose levels but it is expected to be about one foot thick based on current calculations for 0.1 Ci Saltstone. This report documents experiments performed to identify a formulation for the Clean Cap and was requested by Waste Solidification Process Engineering/WSRC[2, 3].

2.1 Background

In the past, grouts made with process water were mixed in the Z-Area process (Readco Processor) and pumped (two centrifugal pumps) into Vault 1 during facility run-in. In addition, Clean Cap grouts were prepared and placed in Vault 1 and on top of the Naval Fuels drums in Vault 4. These Clean Cap grouts contained the 10/45/45, cement/slag/fly ash, premix blend and a water to premix ratios of 0.478 and included Melment 33, a sulfonated melamine polycondensate high range water reducer [4]. The formulation testing for these clean cap mixes was performed by Saltstone engineering and operations personnel and the mixes met the placement requirements of the facility.

Although laboratory scale testing indicated that these Clean Cap mixes should have flowed in the cells problems were encountered during field emplacement. The attempts to place a cap in Vault 1 encountered a placement surface that was very dry, dusty, porous, and covered with hygroscopic salts. The surface in the Naval Fuels cell in Vault 4 did not have any hygroscopic salts but was dry, porous, and dusty.

A review of past attempts to place a clean cap indicate that the surfaces onto which these grout were placed sorbed water from the mix. The result was that water needed function as the carrier fluid was removed from the slurry and the grouts did not flow. The Clean Cap grout mounded and did not flow in Vault 1 and flowed poorly in Vault 4. The same situation was encountered when commercially batched grout/Controlled Low Strength Material were purchased from the Jackson, SC ready mix plant to complete capping in Vault 1. The design mix did not flow and the amount of water in the mix had to be increased above the design maximum to accommodate the dry surface conditions at the direction of BSRI engineering [5].

2.2 Objective

The objective of this task was to design a non radioactive slurry using water (rather than a sodium salt solution), cement, slag and fly ash that can be prepared in the current Saltstone Facility and pumped into the cells in Vault 4 to provide shielding for 0.1 Curie Saltstone. The material requirements for the Clean Cap are listed in Table 2-1.

In addition, mixability in the Readco continuous processor, hydration heat, slurry density, and rheological properties were also considered.

- Mixability was qualitatively evaluated for blender mixing using the Z-Area Laboratory protocol for Saltstone mixing.
- Heat of hydration was not measured and is recommended for Part 2 of this work. However, an attempt was made to provide mix options that generate less heat than the current Saltstone mix.
- Slurry specific gravities were measured since the density is necessary for pumping and shielding calculations. Mixes less dense than Saltstone are less desirable for shielding but better for pumping.
- The rheological properties for Saltstone were measured by several test methods and are provided for comparison to the properties of promising Clean Cap Mix designs.

Table 2-1. Clean Cap Mix Criteria.

Design Criteria	Description
General	
Solid Ingredients	1. Use Saltstone Pre Mix Ingredients if possible. 2. An additional solid component can be accommodated in the fourth silo if necessary.
Mixing Liquid	1. Water which will be staged in the 50,000 gallon Clean Cap Batch Tank (CCBT)
Preparation	1. Use Z-Area dry solids storage, blending, transferring facilities. 2. Prepare the Clean Cap slurry in the Z-Area slurry mixer 3. Pump the Clean Cap slurry to cells in Vault 4 using the same equipment and facilities that will be used for preparing and placing 0.1 Ci Saltstone (peristaltic pump, 3-inch diameter pipe, 25 foot drop, 180 gallons per minute).
Addition of Chemicals to Modify Slurry Properties	1. Chemical admixtures should be suitable for addition to the mixing water staged in tank which will be stirred to achieve uniform admixture blending. 2. Chemical admixtures should be suitable for addition to the mixing water in the tank up to 24 hr prior to processing the Clean Cap. (The SSHT water should have an acceptable minimum hold time of 24 hr.)
Slurry Properties	
Z-Area Slurry acceptance criteria	Flow 75 feet, at least as self-leveling as Saltstone prepared in previous processing runs.
Gel Time	20 to 60 minutes (Longer gel times allow too much settling)
Standing Water	<3 volume percent (minimal)
Set Time	<24 hours
Cured Properties	
Load bearing (>200 psi)	Assumed to be the same as Saltstone

2.3 Limitations

The properties of the surface onto which the Clean Cap will be placed will impact the flow behavior. The potential surface conditions have not been adequately characterized at this time. Variables include but are not limited to temperature, salt content, slope, and wet versus dry conditions.

Flow behavior of cementitious slurries is dependent on the interaction between the solid particles and the interaction between the particles and the liquid phase. Particle, size dispersion, and density along with slurry density and density of the carrier fluid are important parameters that affect the slurry rheology. Saltstone slurry with a water to premix ratio of 0.60 or higher is characterized as a yield pseudoplastic slurry and is shear thinning. Shear imparted to the slurry through mixing, pumping and flow in the transfer line and in the vault affects the apparent viscosity and other rheological properties. In the past, empirical methods consisting of a combination of laboratory gel time and bleed water measurements plus direct observations of the slurry flow in the vaults were used to determine whether a mix was acceptable. (Rheological tests and modeling to predict flow in the vault have not been fully developed.)

Correlation of laboratory results and field results has not been demonstrated for the 0.2 Ci Z-Area process and new equipment (Saltstone hold tank and pump). Laboratory procedures used in this study were applied to the previous Z-Area process (Saltstone hold tank and pumps). Pilot scale testing has not been performed for the new equipment. Consequently laboratory results should be considered as screening results rather than design data.

2.4 Experimental Approach

The approach used to design a clean cap grout was to first identify performance requirements. (Flow and bleed water were identified as the most important requirements.) Various premix formulations and concrete admixtures marketed to modify concrete fresh properties (workability, placement, bleed water, set time) were evaluated to determine whether the slurry could be optimized to meet the flow and bleed water requirements. In addition to the reference premix formulation (10/45/45, cement/slag/fly ash), other lower heat premix formulations were tested. Rheological data were obtained for several of these trial mixes.

Screening studies were performed in the N-Area Civil Engineering Laboratory and rheological data were collected at the Savannah River National Laboratory (SRNL) Aiken County Technology Laboratory (ACTL). The reference Saltstone premix was used for most of the tests.

The logic used to design mixes was as follows:

- Evaluate properties of high-water mix designs similar to those processed in Z-Area.
- Evaluate low-water mixes to reduce bleed water.
    - Add a dispersant to deflocculate the premix particles (micro agglomerates that trap some of the carrier fluid, i.e., water) and thereby reduce the apparent viscosity and yield stress to increase pumpability and flow distance for the lower water mixes.
    - Add a viscosity modifying admixture (thickener) to minimize bleed, for mixes (with dispersant) containing more than the minimum amount of water required to achieve good flow.

- Evaluate low heat mixes containing less slag with and with out dispersants.

3.0 MATERIALS AND EXPERIMENTAL METHODS

3.1 Clean Cap Premix

Four premix compositions were selected for clean cap testing. The reference mix (10/45/45, cement/slag/fly ash) was selected to minimize the impact on operation of the Saltstone facility and to establish a baseline. A cement-fly ash clean cap mix was selected to minimize heat generation. A reduction in raw materials cost can be realized in mixes without slag or with less slag than the reference mix even though the cement content was increased from 10 to 20 or 30 weight percent. A cement-fly ash-low slag mix was selected to minimize heat and provide chemical reduction in the clean cap for stabilization of mercury, chromate, and pertechnetate. A 100 % fly ash mix was also tested in the screening studies. See Table 3-1.

Table 3-1. Pre mix formulations evaluated for the clean cap.

Pre Mix	Portland Cement Type I/II (Holly Hill SC, Holcim Inc.) (wt. %)	Ground Granulated Blast Furnace Slag (Birmingham AL, Holcim Inc.) Grade 100 (wt. %)	Class F Fly Ash (Belews Creek NC, Boral Inc.) (wt. %)
1. Reference	10	45	45
2. Cement-Fly Ash	20	0	80
3. Cement-Fly Ash-Low Slag	20	10	70
4. Fly ash (screening study only)	0	0	100

The reference premix ingredients were blended in large batches in a dry-solids V-Blender. The ingredients for the other premix formulations were weighed in individual batches. The premix ingredients for blends other than the reference mix were prepared in 400 gram batches. The ingredients weights were within 0.2 grams of the target amounts for each ingredient and mixed or premixed in a jar or plastic bag.

3.2 Slurry Property Modifiers

Domestic water from two different sources, SRS N-Area domestic water and Aiken County Talatha Water were used as mixing water for the screening tests and rheological measurements, respectively. The chlorine content of the Talatha Water was reported to be 0.6mg/L [6]. The SRS N-Area domestic water is also chlorinated.

Three types of concrete admixtures were tested to determine whether high flow and minimal bleed water slurries could be achieved relative to a base case (water to premix = 0.5 with the reference premix composition). A list of the admixtures tested are listed in Table 3-2 and included high range water reducers (dispersants), viscosity modifier (thickeners), and fluidifying reagents (air entrainers). The admixtures were added and stirred into the mixing water prior to preparing the slurries.

Table 3-2. Admixtures tested in the screening studies.

Admixture Effect	Vendor	Product	Targeted Properties	Chemical Composition	Density (g/mL)
HRWR (Type F)	W. R.Grace	Adva 530	High efficiency polycarboxylate based Superlasticizer	• Polycarboxylate (25 – 50%)	1.07
		Adva 540	High efficiency polycarboxylate based Superlasticizer	• Polycarboxylate (10 – 25%)	1.05
	IAIC	SP1000	Superplasticizer (copolymer)	• Unknown	
	Sika	Sika 2100	High efficiency polycarboxylate based Superlasticizer	• Polycarboxylate	1.07
Viscosity Modifying Admixture	Master Builders (Degussa)	Reomac VMA 450	Cement dispersing agent Viscosity modifier (increase viscosity, increase thixotropy, control bleeding)	• hexylene glycol • modified cellulose ether	1.21
Set Retarder (Hydration Stabilizer)	W. R. Grace	Daratard 17	Set retarder	• Sodium o-phenylphenol (< 1%) • Corn Syrup, • Calcium Lignosulfonate	1.17
		Recover	Hydration stabilizer Water reducing and retarding admixture	• Polycarboxylate (25 – 50%) • Sodium Gluconate • Sucrose	1.18
Other	Moxie International	Moxie 1800	Water reducer	• Unknown	1.08
	IAIC	AEVR	Surfactant	• Unknown	1.03
	DOW	Methocel	Reduce bleed and increase flow	• Hydroxyproply methylcellulose (85 – 99%) • Sodium chloride (0.5 – 5%) • Proprietary plyglycol, carboxylic acid, and aldehyde	Powder

3.3 Slurry Rheology Characterization

3.3.1 Mixability

A quantitative test is not available to evaluate mixability. However, Saltstone Operations personnel have considerable experience mixing Saltstone and have mixed Clean Cap formulations with water to premix ratios of 0.47. These operational experiences along with general observations on laboratory samples were used to judge mixability.

Two mixing techniques were used in this study to achieve two different shear conditions which is important for a shear thinning slurry. Most of the mixes were prepared in a Blender according to the Z-Area laboratory mixing procedure [7]. Selected mixes were mixed by stirring in a beaker. (Redesign of the Z-Area grout transfer system from centrifugal pumps to a peristaltic pump may impact the slurry properties due to differences in the imparted shear.)

3.3.2 Bleed Water, Specific Gravity, Compressive Strength

Bleed water (standing water) and specific gravity of the Saltstone and the Clean Cap slurries are important parameters for engineering design calculations. Both properties were measured using the Z-Area procedure [7]. Compressive strength measurements were also made on several of the samples originally cast in 2 x 4 inch cylinders for bleed water tests. The purpose of the compressive strength testing was to demonstrate that the samples have the potential to reach 200 psi after curing for 28 days. The age of the samples tested ranged from 7 to 21 days. Only one measurement is reported because the supply of cement, slag and fly ash was not sufficient to prepare triplicate compressive strength samples.

3.3.3 Fluid Properties

The fluid properties of the Clean Cap slurries are relevant to the following functions in the Z-Area process:

- Mixing
- Transfer via pumping
- Flow in the vault
- Response time for upset conditions such as mixer and pump plugging.

Each of these functions requires a unique set of rheological data and hence unique measurements. Three separate tests which are described below were developed to provide design data relevant to slurry pumping, slurry flow in the vault, and response time and are described below. A test for mixing is not available. Mixes that were difficult to mix stopped the blender when the solids were added to the water. Mixes that were easy to mix quickly incorporated the solids into the water.

3.3.3.1 Pumpability

The rheological properties of the Clean Cap slurries were characterized using a Haake Rheometer Model RS-600 equipped with a stationary serrated sample cup (outer cylinder) and a rotating serrated Z38 bob (inner cylinder). This equipment uses a serrated coaxial cylindrical geometry. The flow in the annular gap between the two concentric cylinders was characterized by measuring the torque and speed of the inner cylinder. The torque readings were converted to shear stress and the speed to shear rate.

Flow curves (up and down) were generated over a shear rate range of 0 to 300 sec^{-1}. Each curve took two minutes to accelerate/decelerate. After accelerating to 300 sec^{-1}, the shear rate was held for 30 seconds prior to decelerating. Flow curves were generated for fresh Saltstone slurry samples immediately after mixing in the blender or by stirring in a beaker. The curves were analyzed using rheological models. Based on the shapes of the down curve, a flow rheological model was used for regression of the data.

Two flow models were apparent:

- **Bingham Plastic Fluid Model:** Pseudoplastic flow (shear thinning) behavior at water to premix ratios above about 0.40. Some of the pseudoplastic slurries displayed either one or more of the following additional features and were characterized as follows:
    - Pseudoplastics which have a yield stress are referred to as Bingham Plastics.
    - Pseudoplastics with thixotropic behavior which implies that the gel structure, once disrupted by shear, can reform at rest. A hysteresis in the shear rate – shear stress indicates thixotropy. (Cement slurries are not truly thixotropic because the chemical reactions responsible for the formation of structure are not reversible. However, as long as structure can be disrupted by shear similar structure will form until all of the material has completely reacted.)
- **Power Law Fluid Model:** Dilatant flow (shear thickening) behavior at water to premix ratios below 0.40 for mixes containing dispersants.

For slurries that exhibited pseudoplastic behavior, the Bingham Plastic model was used to calculate the plastic viscosity and yield stress. Essentially the entire range of shear stress-shear rate data was used in these calculations. Equations used to calculate the plastic viscosity and yield stress using the shear stress-shear rate data are presented elsewhere [8].

For slurries that exhibited dilatant flow behavior, the Power Law model flow coefficient, K, and the power law exponent, n, were calculated. Equations used to calculate these parameters are presented elsewhere [8].

3.3.3.2 Flow in Vault

The samples tested as described in Section 3.3.1 were allowed to rest in the rheometer without any shear for at least 20 minutes. Afterwards a second flow curve was generated at a slower shear rate, 0 to 10 sec^{-1}. Flow curves generated in this way are thought to be more relevant to the properties of material at the edge of the flow front advancing in the vault than flow curves generated at higher shear rates immediately after mixing.

At this time it is not possible to correlate the rheological properties calculated from these data with actual flow behavior because a correlation between actual flow in the vault and laboratory data does not exist. Consequently, these flow curves are available for discussion but were not presented in this report. They may be useful for development of a test method to evaluate flow in the vault at a later time.

A simple flow measurement similar to ASTM D-6103 but using 2 x 4 inch test cylinders rather than 3 X 6 inch clyinders, was used to evaluate the self leveling and flow ability of slurries prepared for the admixture screening tests described in Section 3-4 [9]. Although results from this test have not been correlated with field data, the test provides a visual indication for the potential of the slurry to flow in the vaults.

3.3.3.3 Upset Condition Response Time: Static Gel Time

Gel time and set time can be measured under static or dynamic conditions. Hydration reactions between the cement particles and water result in the formation of new particles which is referred to as the development of structure in the slurry. As structure forms the slurry becomes less and less fluid until it gels and becomes a plastic solid similar to compacted clay soil. As more structure forms the plastic material will become more rigid. Set is a condition where the material is resistant to penetration at a given force. The magnitude of the force depends on the relevant requirements.

For Saltstone, static gel time has been used to estimate the recovery time in the event of a pump malfunction. It is an indication of the maximum amount of time the pumps could be inoperable before the slurry developed enough structure to prevent fluid response to pressure. It has also been used along with operating experience to estimate Saltstone flowability in the vaults.

In this study static gel time was measured using a Haake Rheometer Model RS-150 equipped with a four-blade vane (FL22) rotating at 1 revolution per hour. The data collected was for minimal shear and thereby approximates static conditions. The test conditions, amount of slurry and placement of the vane in the cup were kept the same for each sample.

Because gelling is a process associated with progressive development of structure in the slurry, identification of an exact gel time is somewhat arbitrary. The point at which the slope of the shear stress versus time curve increases is a reasonable indicator of the static gel time. This typically occurs after the first indications of vane slipping are noticed as indicated by the increased amplitude of the variation in the rotational speed [8]. Both indicators occur over a few minutes and these data are consistent with the gel time obtained from the pour test performed at 10 to 15 minute time intervals.

3.4 Admixture Screening Studies

Commercially available concrete admixtures were tested to evaluate effectiveness of increasing flow and decreasing bleed water. Screening studies were performed to evaluate the effects of several types of admixtures on the clean cap slurries. The reference premix formulation (10 wt% cement, 45 wt% slag, 45 wt% fly ash) was used for most of the admixture testing. However, some tests were also performed on the low slag mixes.

3.4.1 Slurry Preparation and Testing

Slurries were prepared in a blender (mixed for 1 minute at low speed and then at 2 minutes at medium speed) or by stirring with a spatula in a beaker. Mixability was described qualitatively. Screening tests were performed in which flow was evaluated by a method similar to ASTM D-6103 test using a 2 x 4 inch form and a glass plate rather than a 3 x 6 inch form. The spread on the glass plate was reported as flow in inches. Completely self leveling slurries flowed off the plate and had a flow of greater than 12 inches (the size of the plate). See Figures 3-1 and 3-2. The remainder of each sample was cast in 2 x 4 inch cylinders and bleed water was measured after 24 hours. Gel time was estimated by checking pourability per the Z-Area pour test [7] at various time intervals after casting. Compressive strength was measured on the material in the bleed water cylinders which were capped and stored at ambient temperature. Compressive strength measurements were made after at least 7 days of curing to confirm that the strength requirement (200 psi after 28 days curing) was or could be met. (These screening tests were performed in the N-Area Civil Engineering Laboratory.) See Figures 3-1 and 3-2.

Figure 3-1. Slurry with a 6 inch flow per modified ASTM D6103. (Not Self Leveling)

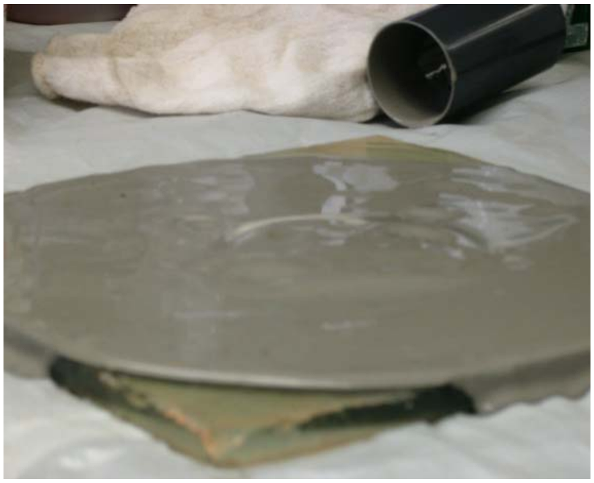


Figure 3-2. Self-leveling slurry with more than 12 inches of flow.

4.0 RESULTS

4.1 Trial Mixes without Admixtures

The first set of tests was designed to measure and compare properties of Clean Cap slurries made with the reference premix and water (no admixtures). The water to premix ratio was varied from 0.5 to 0.7, and two different mixing techniques were used. One laboratory mixing technique (mixing in a blender for 3 minutes) has been qualitatively correlated with the appearance of the product discharged in to Saltstone vaults during successful processing. The other technique (hand mixing for 3 minutes) was selected to simulate mixing at lower shear conditions for comparison purposes. In the past, slurry produced by the Readco Processor and collected upstream of the centrifugal pumps in the Z-Area process room visually resembled, or was even thicker than, the material made by stirring in a beaker.

The rheological properties of clean cap slurries containing the reference premix and no admixtures are compared to the properties of a Saltstone slurry prepared from the reference premix and a salt solution containing 4.5M sodium salts. See Table 4-1. Flow curves used to determine the flow behavior and to calculate plastic viscosity and yield stress are provided in Figure 4-1.

Yield-Pseudoplastic flow behavior was characteristic for the slurries made with water to premix ratios between 0.4 and 0.7. In other words the slurries are shear rate thinning and require a finite amount of applied stress in order to flow. In addition, the rheological properties of these slurries are time dependent and irreversible over extended time intervals because irreversible chemical reactions (hydration of the suspended particles) occur.

A Bingham plastic flow model and corresponding equations were used to calculate the apparent viscosity and yield stress from the shear stress-shear rate data plotted to generate the flow curves. The ranges of shear rate values used in the curve fitting are also listed in Table 4-1. Apparent viscosities ranged from 14 to 152 cP and yield stresses ranged from 2.6 to 18.4 mPa. Bleed water was also measured for these slurries. Results ranged from 0.6 to 14.8 volume percent over the range of water to premix ratios tested. Results for plastic viscosity, yield stress and bleed water are plotted in Figures 4-2 to 4-4.

Table 4-1. Clean Cap Trial Mixes Made with Reference Premix and Water [8].

Sample ID	W/P	Mixing System	Vol. % Bleed Water	Gel Time (min)	Rheology					
					Yield Stress (Pa)	Plastic Viscosity (cP)	Curve Fitting for Bingham Plastic Approximation		Flow Behavior (Flow Curve)	Comments On Flow Curves
							R^2	Fitted $\dot{\gamma}$ (sec^{-1})		
SSW1	0.60	Blender	6.1	40	4.7	25	0.990	20-300	Yield-Pseudoplastic	No thixotropic (TH) behavior, slight power law (PL) behavior at low shear rate.
SSW2	0.60	Stir	N/M	30	7.4	56	0.991	20-300	Yield-Pseudoplastic	TH behavior, more PL behavior than SSW1.
SSW3	0.07	Stir	10.0	N/M	3.5	25	0.993	10-300	Yield-Pseudoplastic	Slight TH behavior. Particle jamming impacting flow curve.
SSW4	0.70	Blender	14.8	N/M	2.6	14	0.991	20-300	Yield-Pseudoplastic	No TH behavior, slight PL behavior at low shear rate.
SSW5	0.50	Stir	0.6	30	18.4	152	0.996	60-300	Yield-Pseudoplastic	Very evident TH behavior, PL behavior. Particle jamming.
SSW6	0.50	Blender	2.2	N/M	11..5	53	0.994	40-300	Yield-Pseudoplastic	Very PL at low shear rate. Slight TH behavior.
Reference Saltstone 4.5M Na	0.60	Blender	<1	25	8.5	36	0.998	20-300	Yield-Pseudoplastic	Thixotropic
Reference Saltstone 4.5M Na	0.60	Stir	<1	10	8.1	90	0.999	20-300	Yield-Pseudoplastic	Thixotropic

N/M = Not Measured

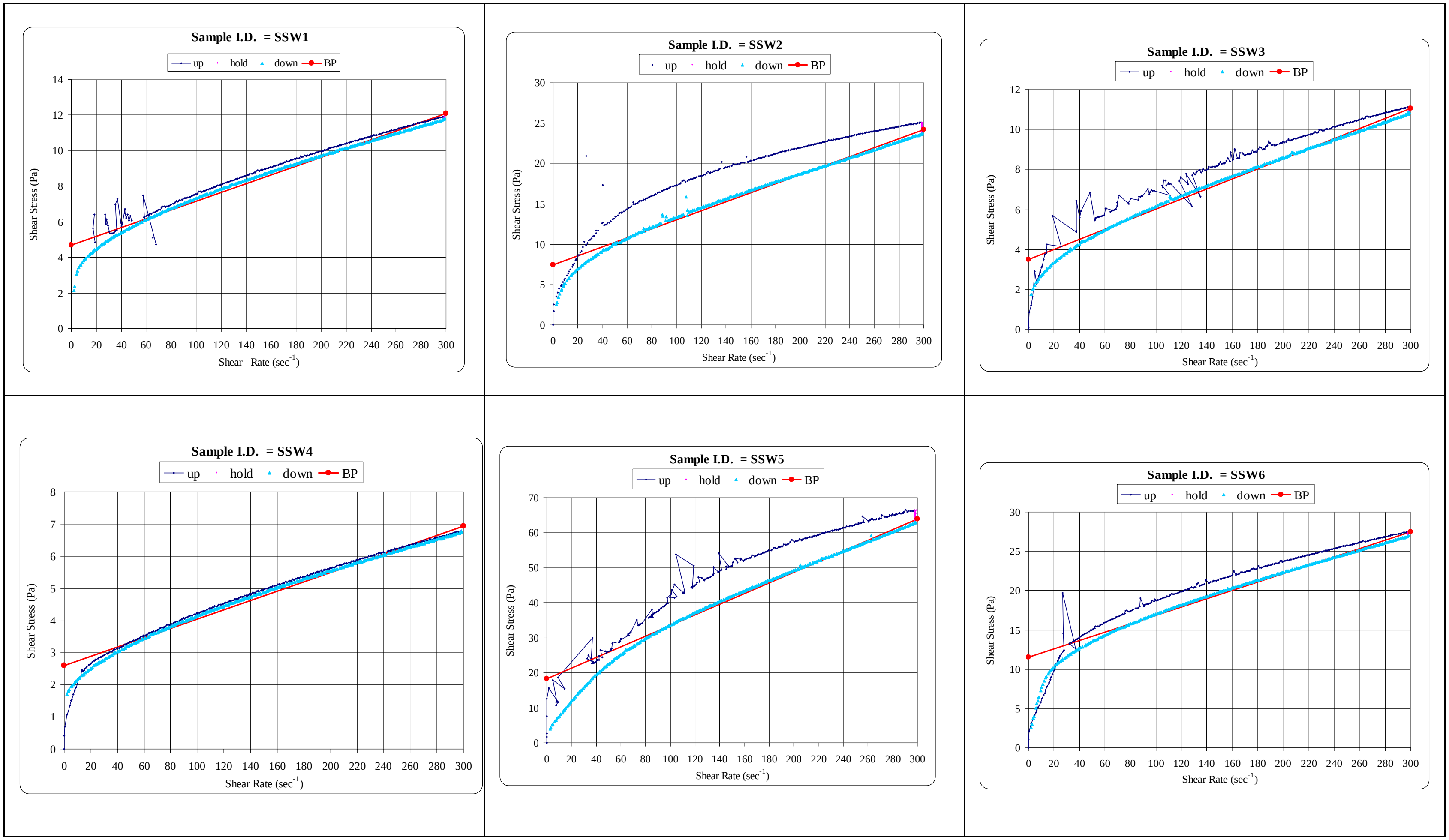


Figure 4-1. Flow curves for Clean Cap slurries prepared with water/reference premix ratios between 0.45 and 0.60.

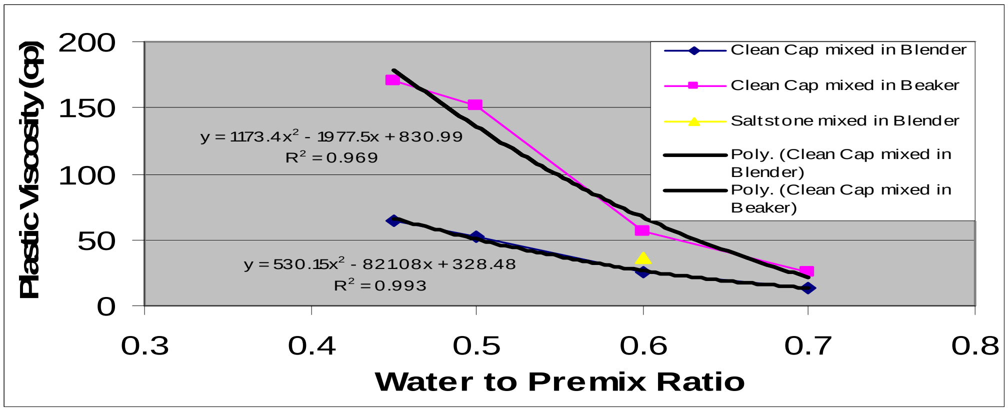


Figure 4-2. Plastic viscosity versus water to premix ratio for Clean Cap Mixes made with the reference premix and 4.5M Na Saltstone.

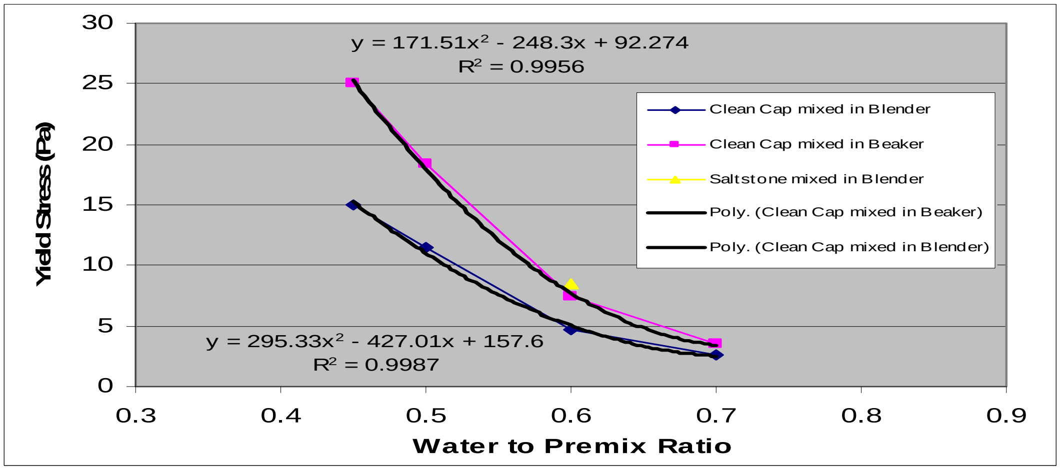


Figure 4-3. Yield stress versus water to premix ratio for Clean Cap Mixes made with the reference premix and 4.5M Na Saltstone.

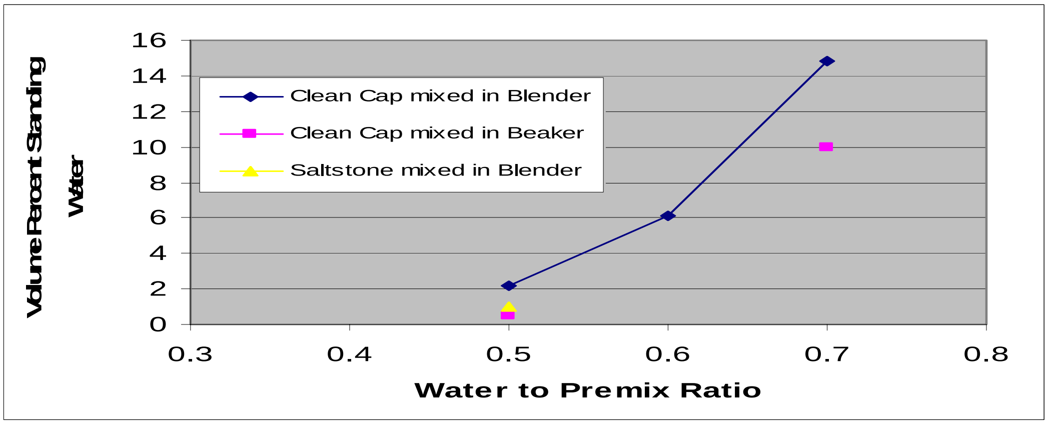


Figure 4-4. Standing (bleed) water versus water to premix ratio for Saltstone and Clean Cap Mixes made with the reference premix.

4.2 Admixture Screening

Several admixtures were screened using the reference premix formulation (10, 45, 45 wt% cement, slag, fly ash, respectively). Mixability was evaluated by simple observation. Most mixing was performed in a blender. A few mixes were made by stirring in a beaker. A flow test was used to compare slurry rheologies. Bleed water and gel time were also measured.

4.2.1 Baseline Reference Premix

Baseline data for reference premix without admixtures were generated and are listed in Table 4-2. Mix Numbers 3 and 4 met the criteria for the Clean Cap. All of the slurries were made in a blender and the mixability improved as the water to premix ratio increased from 0.40 to 0.60. All of these mixes gelled in 45 to 60 minutes and set in less than 12 hours and displayed bleed water. Only the mix with a water to premix ratio of 0.60 had a flow of 12 inches and was self-leveling. At lower water to premix ratios, less flow (spread) was observed on the glass plate.

The amount of bleed water was between 2 and 5 volume percent after 1 hour. Surprisingly, the volume of bleed water was not a direct function of the water to premix ratio. Also the amount of bleed water after one hour did not correlate with the amount of bleed water measured for the samples prepared for rheological measurements (Compare bleed water results in Tables 4-1 and 4-2).

The effect of mixing technique was evaluated at a water to permix ratio of 0.50. Sample No. 2 prepared in the blender (higher shear) flowed better and generated more bleed water than sample No. 5 which was prepared in the beaker by stirring.

4.2.2 Effect of High Range Water Reducers on Reference Premix

Several Type F high range water reducers (HRWR) were evaluated in an attempt to achieve flow at lower water to premix ratios with the overall objective of reducing bleed water. (The HRWRs were added to the mixing water prior to adding the reference premix blend.)

The HRWRs produced slurries that flowed better (per ASTM D-6103) than mixes without the HRWRs for given water to premix ratios. HRWR doses between 0.2 and 1.43 g per 400 g of premix were tested. The higher doses did not improve mixability. A HRWR dose corresponding to 0.05 weight percent of the premix was effective in improving flow and reducing bleed at water to premix ratios above 0.30.

At water to premix ratios below 0.40, mixing in the blender was difficult. Therefore low water mixes with HRWR were not recommended at this time even though the bleed water was minimal and flow was good. At water to premix ratios up to 0.50, mixes containing HRWR generated the same or less bleed water than mixes without HRWR. Results for two of these admixtures, ADVA 540 and Sika 2100 are listed in Tables 4-3 and 4-4, respectively. Mix Numbers 6 and 7 (Adva 540) and Mix Number 9 (Sika 2100) met the Clean Cap criteria. Gel time and set time were not affected in the mixes containing the HRWRs tested.

Table 4-2. Properties of Clean Cap slurries made with the Saltstone premix.

Mix No	Admixture	Cement/Slag/Fly Ash (Wt.%) water/premix	Cement (g)	Slag (g)	Fly Ash (g)	Water (g)	Mixability	Flow (in.)	Gel Time (min.)	Bleed Water @1 hr (vol. %)	Set Time (hr.)	Observations Compressive Strength After 7 days
20	none	10/45/45 0.4	40	180	180	160	Mixed but thick	Slump No flow	NA	~2 %	<12	Thick slurry which was difficult to mix in blender. 2082 psi after 21 days
1	none	10/45/45 0.45	40	180	180	180	Good	9	< 30	~ 3 %	<12	482 psi
2	none	10/45/45 0.5	40	180	180	200	V. Good	10.5	30 to 45	~5 %	<12	Almost self leveling except for mounding or segregation in center of pour 374 psi
3	none	10/45/45 0.55	40	180	180	220	V. Good	11.25	~ 45	~ 2 %	<12	353 psi
4	none	10/45/45 0.6	40	180	180	240	V. Good	12	~ 60	~ 3 %	<12	Mix continued to settle (bleed but after 24 hr there was slightly less than 3 % bleed) 232psi
5	none	10/45/45 0.5	40	180	180	200	Stir in Beaker	~10	30 to 45	~1 %	<12	Beaker mixing 291 psi

Shading indicates mixes that meet the criteria for a Clean Cap.

Table 4-3. Slurry properties of mixes containing ADVA 540.

Mix No.	Admixture Adva 540 (g/400g premix)	c/s/fa water/premix	Cement (g)	Slag (g)	Fly Ash (g)	Water (g)	Mixability	Flow (in.)	Gel Time (min.)	Bleed Water @ 24 (hr) (vol%)	Set (hr.)	Observations Compressive Strength After 14 days
34	1.04g	10/45/45 0.3	40	180	180	120	Difficult	>12	>30	<0.5	<24	Ribbon to stream flow 3257 psi
30	1.43g	10/45/45 0.3	40	180	180	120	Difficult	>12	>30	<0.5	<24	Stream Flow, 100% self Leveling 3006 psi
32	0.75g	10/45/45 0.35	40	180	180	120	OK	7.75	Not tested	Not tested	Not tested	Ribbon flow, sticky 1984 psi
24a	0.48g	10/45/45 0.4	40	180	180	160	Very Difficult	7	Not tested	Not tested	Not tested	3194 psi
24b	0.84g total (0.48+ 0.36)						Already mixed when second dose added	~12	35+	1 %	Not tested	After 2nd admixture addition achieved stream flow 2467 psi
6	0.2 g	10/45/45 0.45	40	180	180	180	Good	>12	45 to 60	Trace @ 1 hr	<12	454 psi after 7 days
7	0.2 g	10/45/45 0.50	40	180	180		V. Good	> 12	45 to 60	~ 1 % @ 1 hr	<12	384 psi after 7 days

Shading indicates mixes that meet the Clean Cap criteria.

Table 4-4. Slurry properties of mixes containing Sika 2100.

Mix No.	Admixture Sika 2100 (g/400 g premix)	Cement/Slag/ Fly Ash water/premix	Cement (g)	Slag (g)	Fly Ash (g)	Water (g)	Mixability in Blender	Flow (in.)	Gel Time (min.)	Bleed Water @ 1 hr (vol.%)	Set Time (hr.)	Observations Compressive Strength after 14 days
38	1.0g	10/45/45 0.3	40	180	180	120	Difficult	>12	>45	Yes	<12	Stream flow; very fluid at 30min; very pourable after 45min 2314 psi
42	0.5g	10/45/45 0.3	40	180	180	120	Difficult	>12	>25	Yes	<12	Fluid to slight ribbon. Less circulation pattern in pour. 2835 psi
8	0.3g	10/45/45 0.3	40	180	180	120	Difficult	>12	~ 60	4 %	<12	3272psi
43	0.25g	10/45/45 0.3	40	180	180	120	Difficult	~ 12	~30	Trace	<12	Thicker than 42. 2344 psi
9	0.2	10/45/45 0.45	40	180	180	180	Good	>12	~ 40	~ 2 %	<12	411 psi after 7 days
10	0.2	10/45/45 0.50	40	180	180	250	V. Good	>12	~ 40	~ 2 % ~3.5% @ 2 hr	<12	Not measured
48	1.0g	10/45/45 0.3	40	180	180	120	Difficult Stir in Beaker	>12	N/A	N/A	N/A	Stream flow but not as fluid as mixer. Flow test ran off board.

Shading indicates mixes that meet the Clean Cap criteria.

4.2.3 Effects of Retarders, Air Entrainers and Other Admixtures on the Reference Premix

One set retarder Daratard 17 and a melamine sulfonate water reducer were tested in the reference mix. Neither of these admixtures improved the flowability of the Reference Clean Cap formulation. These admixtures were tested at low water to premix ratios to evaluate improvement in flow.

Two other admixtures were evaluated. Moxie 1800, Mix Number 37, and AEA, Mix Number 23, resulted in slurries that met the Clean Cap criteria. Moxie 1800, marketed as a means of reducing bleed and porosity, produced positive results compared to the reference Clean Cap without admixtures. AEA, an air entraining admixture also improved flow compared to formulations without the admixture. See Table 4-5.

4.2.4 Alternative Premix Formulations

Three alternative premix formulations were evaluated to address potential improvements such as reduced heat of hydration and reduced materials cost. The first alternative mix contained only Class F fly ash and had a low water to solids ratio (Mix Number 29). A HRWR was added to enhance flow at the low water to solids ratio. This water-fly ash slurry was very flowable and did not gel. However, the fly ash particles settled out of suspension and compacted with time. This slurry also continued to settle and express bleed water for more than a week. This type of mix is not suitable for the Clean Cap but may be suitable for cold run-in of the new Z-Area equipment. Results are listed in Table 4-6.

The second alternative premix formulation consisted of 20 weight percent cement and 80 weight percent Class F fly ash. Results of screening tests are provided in Table 4-7. Since mixing problems were encountered in previous testing at water to premix ratios less than 0.4 and since the lowest water to premix ratio slurry processed in the Saltstone facility is 0.478, a minimum water to premix ratio of 0.45 was selected for this series of tests. At water to premix ratios of 0.45 and above, all of the Clean Cap criteria were met except for bleed water. Even at a water to premix ratio of 0.45, 6 volume percent bleed water was generated within one hour after casting. In addition, these slurries continued to settle and produce more bleed water for several hours.

The third alternative premix formulation evaluated contained 20 weight percent cement, 10 weight percent slag and 70 weight percent fly ash. Results are listed in Table 4-8. The results are similar to those for the 20/80 cement-fly ash mixes except less bleed water was generated for a given water to premix ratio. Although Mix Number 75 did not met bleed water criteria after 1 hour (>6 volume percent bleed water), the same composition prepared as a duplicate, Number 67a, met the Clean Cap criteria after 3 days (2.5 volume percent bleed water).

Table 4-5. Slurry properties of mixes prepared with set retarders and other admixtures.

Mix No.	Admixture	Cement/Slat/ Fly Ash water/premix	Cement (g)	Slag (g)	Fly Ash (g)	Water (g)	Mixability	Flow (in.)	Gel Time (min.)	Bleed Water @24 hr Vol %	Set (hr)	Observations
22	Daratard 19 0.85g	10/45/45 0.40	40	180	180	160	Difficult	7	~45	Not tested	Not tested	No benefit to flow or bleed water
26 B	Daracem 19 3.45g	10/45/45 0.30	40	180	180	120	Very stiff but mixed to a stiff paste after 2 min in blender	Not pourable	Not tested	Not tested	Not tested	Repeated test with same results Possibly bad sample of Daracem
41	Moxie1800 2.00g	10/45/45 0.30	40	180	180	120	Poor	>12in	N/A	N/A	N/A	Moxie gives minimal foam
37	Moxie 1800 1.50g	10/45/45 0.5	40	180	180	200	Good	>12in	??	2.5%	N/A	Flowed well ; dimpled center of 5”center Bleed
23	AEA 0.61g	10/45/45 0.50	40	180	180	200	Good	>12	~45	1.2%	<24	Self leveling. Very pourable Air bubbles in saltstone slurry

Shading indicates mixes that meet the Clean Cap criteria.

Table 4-6. Slurry properties of a fly ash-water mix containing a HRWR.

Mix No.	Admixture	Cement/Slag/ Fly Ash water/premix	Cement (g)	Slag (g)	Fly Ash (g)	Water (g)	Mixability	Flow (in.)	Gel Time (min.)	Bleed Water Vol % @24 hr	Set (hr)	Observations
29	**Adva 530** 1.43g	0/0/100 0.35	0	0	400	140	OK	>12	No gel	11	No set	Stream flow 100% self leveling, Bleed started immediately

Shading indicates mixes that meet the Clean Cap criteria.

Table 4-7. Slurry properties of cement-fly ash mixes with and without HRWR.

Mix No.	Admixture	Cement/Slag/ Fly Ash water/premix	Cement (g)	Slag (g)	Fly Ash (g)	Water (g)	Mixability	Flow (in.)	Gel Time (min.)	Bleed Water (vol.%)	Set (hr)	Observations
72	0	20/0/80 0.45	80	0	320	180	Good	>12	~60	~8 @ 1hr	<12	Stream pour
73	0	20/0/80 0.50	80	0	320	200	V. Good	>12	~60	~10 @ 1hr	<12	Immediate bleed
74	0	20/0/80 0.55	80	0	320	220	V. Good	>12	~60	~12 @ 1hr	<12	Immediate bleed
70	Sika 2100 0.5	20/0/80 0.40	80	0	320	160	V. Good	>12	~60	>6%	<12	Stream flow with body

Shading indicates mixes that meet the Clean Cap criteria.

Table 4-8. Slurry properties of cement-low slag-fly ash mixes.

Mix No.	Admixture	Cement/Slag/ Fly Ash water/premix	Cement (g)	Slag (g)	Fly Ash (g)	Water (g)	Mixability	Flow (in.)	Gel Time (min.)	Bleed Water Vol %	Set (hr)	Observations
66a	Sika 2100 0.6g	20/10/70 0.40	80	40	280	160	Good	12	45 to 60	Yes	Not tested	Still pourable after one hour
67a	0	20/10/70 0.45	80	40	280	180	Good	~12	>60	2.5 after 3 days	<24	Fluid and still pourable after 1 hour
75	0	20/10/70 0.45	80	40	280	180	Good	>12	~40	~6 @1hr	<12	Immediate bleed
76	0	20/10/70 0.50	80	40	280	200	V. Good	>12	~40	~8 @ 1hr	<12	Immediate Bleed
77	0	20/10/70 0.55	80	40	280	220	V. Good	>12	~40	~10 @1hr	<12	Immediate Bleed

Shading indicates mixes that meet the Clean Cap criteria.

4.3 Rheological Properties of Low Water Reference Premix Clean Cap Formulations

Rheological property data were collected for mixes containing the reference premix ingredients and proportions (10/45/45, cement/slag/fly ash by weight) and low water to premix ratios (w/premix = 0.35). If mixable in the Z-Area equipment, these mixes have the potential to produce no bleed water and be self-leveling in the vault. (Refer to all mixes in Table 4-1 and Mixes 3 and 4 in Table 4-2.)

In order to achieve self leveling flow, HRWRs, ADVA 540 and Sika 2100, were added to the mixing water. The rheological properties of these low water mixes are listed in Table 4-9 and flow curves are provided in Figure 4-5. The flow curves indicate that these slurries are shear rate thickening, i.e., dilatant. Consequently, the shear stress-shear rate data were fitted to a Power Law Model. The flow coefficient, K, and the power law exponent, n, for this type of model are listed in Table 4-9.

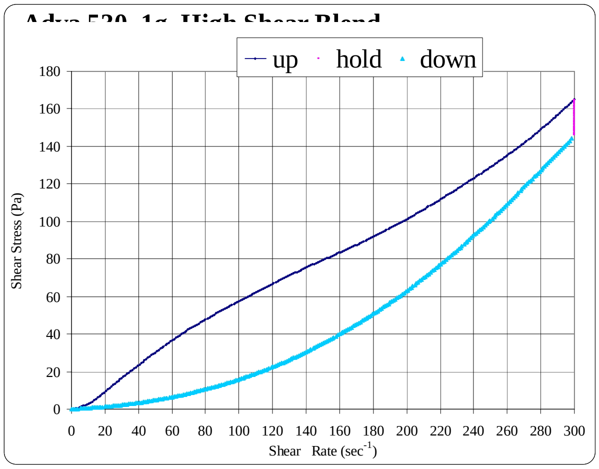
4.4 Rheological Properties of Alternative Premix Clean Cap Formulations

The rheological properties of selected mixes containing low heat alternative premix ingredients were also measured. At water to premix ratios between 0.40 and 0.50, these mixes are yield pseudoplastic slurries. Rheological properties are listed in Table 4-10. The solids in these slurries settled quickly and consequently more bleed water was generated than at comparable water to reference premix ratios. Flow curves for these slurries are provided in Figure 4-5.

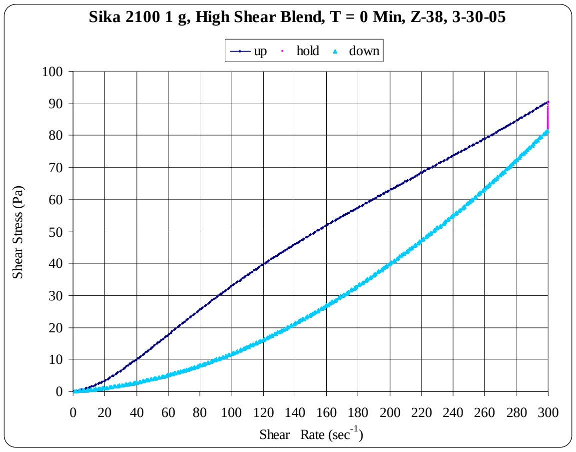
Table 4-9. Rheological data for low water formulations made with the Reference Premix and HRWR admixtures.

Mix No.	**Admixture**	**c/s/fa water/premix**	**Cement (g)**	**Slag (g)**	**Fly Ash (g)**	**Water (g)**	**Mixability**	**K (Pa-sec^n)**	**n**	**Curve fitting for Power Law approx R^2**	**(Flow Curve) Fitted $\dot{\gamma}$ (sec^{-1})**	**Flow Behavior**	**Comments On Flow Curves**
106 Blender	Adva 540 1g	10/45/45 0.35	40	180	180	120	Difficult	0.00121	2.052	0.9998	0-300	Dilatant	Dilatant but shear thinning at constant shear
107 Blender	Sika 2100 1g	10/45/45 0.35	40	180	180	120	Difficult	0.00350	1.763	1.000	0-300	Dilatant	Dilatant but shear thinning at constant shear
108a Stirred in Beaker	Sika 2100 1g	10/45/45 0.35	40	180	180	120	Difficult	0.00120	2.144	1.000	0-300	Dilatant	Dilatant but shear thinning at constant shear

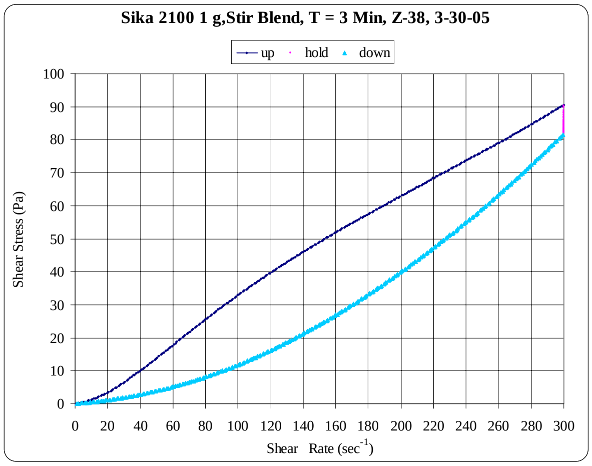
Bleed water was less than 2 volume percent after 1, 2, and 24 hours for all mixes.



(a) Mix 106



(b) Mix 107

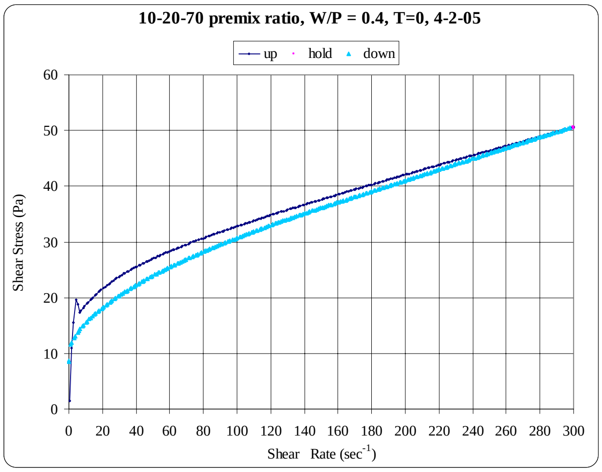


(c) Mix 108a

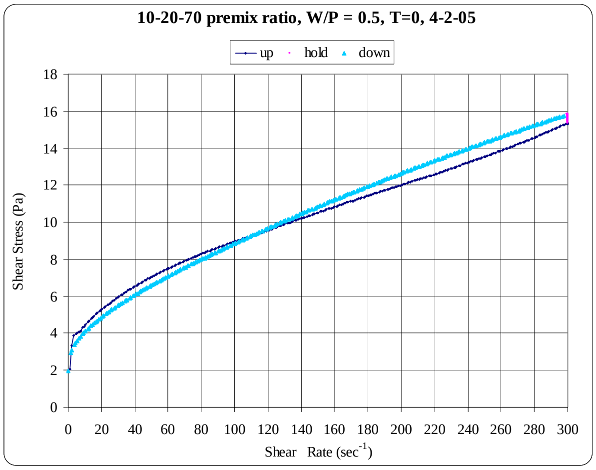
Figure 4-5. **Flow curves for slurries made with the HRWRS, the reference premix and a w/premix = 0.35.**

Table 4-10. Rheological data for low heat mixes without admixtures.

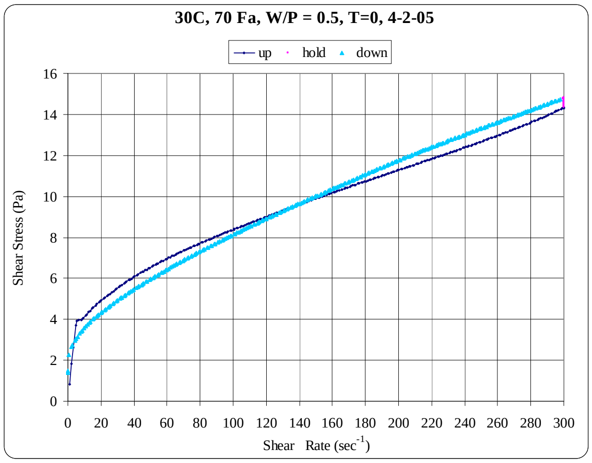
Mix No.	Admixture	Cement/Slag/ Fly Ash water/premix	Cement (g)	Slag (g)	Fly Ash (g)	Water (g)	Mixability	Yield Stress (Pa)	Plastic Viscosity (cP)	Curve fitting Bingham plastic approx R^2	(Flow Curve) Fitted $\dot{\gamma}$ (sec^{-1})	Flow Behavior	Comments On Flow Curves
103	0	20/10/70 0.40	80	40	280	160	Good	18.5	111	0.9877	10-300	Yield-Pseudoplastic	Solids settled
104	0	20/10/70 0.50	80	40	280	200	V. Good	4.6	39	0.9900	5-200	Yield-Pseudoplastic	Solids settled
105	0	30/0/70 0.50	120	0	280	200	V. Good	4.1	37	0.9902	5-200	Yield-Pseudoplastic	Solids settled



(a) Mix 103



(b) Mix 104



(c) Mix 105

Figure 4-6. Flow curves for low heat slurries.

5.0 DISCUSSION

5.1 Previous Clean Cap Mixes

Past attempts to place Clean Caps using slurries prepared in the Saltstone facility were unsuccessful. A review of these attempts indicated that the mix designs met the laboratory criteria for Saltstone but did not flow well in the vaults. In order to meet the criteria, the mixes were designed with a low, 0.478, water to premix ratios. This relatively low water to premix ratio did not take into account the conditions of the surface onto which the Clean Cap was placed. The dry porous surfaces in Vaults 1 and 4 pulled water out of the Clean Cap mix and limited flow. The same conditions were encountered when grout, purchased from a ready mix plant, was substituted for the Clean Cap slurry produced in Z-Area. Additional water had to be added to overcome the effects of the base material and ambient conditions [5].

The past attempts to formulate and place Clean Caps are examples of the poor correlation between laboratory test results and actual placement (field test) results. The slurry tests performed in Z-Area do not accurately predict flow in the vault because:

1. They do not take into account actual placement conditions.
   Characteristics of the placement surface (wet, dry, dusty, porous, variable temperature) effect flow of aqueous slurries in which the solid particles are reacting during the time in question.
2. The only evaluation of rheology used in the Z-Area Laboratory is the static gel time test which is only an empirical indication of flow in the vault.

The past attempts at placing Clean Cap slurries did provide a basis for identifying 0.478 as the lowest water to premix ratio processed in the facility. Since difficulty was encountered in laboratory blender mixing of low water mixes (water/premix <0.35) a condition was added to criteria for designing a new Clean Cap slurry. Based on current processing experience, the water to premix for a clean cap formulation must be greater than 0.478 to assure mixability. If slurries with lower water to premix ratios are demonstrated to be processible in the Saltstone Facility, improved flow and less bleed water will be achieved with deflocculated low water to premix formulations containing HRWR admixtures.

5.2 Clean Cap Options

Options were investigated to evaluate potential improvements to the Reference Cap and to provide operational flexibility. The options are summarized below and include two different types of flow behavior and three different premix compositions:

Flow Behavior

1. Yield Pseudoplastic (flocculated solids with water to premix >0.50)
2. Dilatant (deflocculated solids with water to premix <0.40)

Premix Compositions

1. Reference Clean Cap (10/45/45 cement/slag/fly ash, respectively by weight)
2. No Slag Premix (20/80 cement/fly ash, respectively by weight)
3. Low Slag Premix (20/10/80 cement/slag/fly ash, respectively by weight)

Past operating experience in the Saltstone facility was the basis for recommending the reference premix (10/45/45 cement/slag/fly ash) with a water to premix ratio of 0.60 as the Clean Cap mix design. Mixability of slurries with a water to premix ratios less than 0.478 has not been demonstrated. Processing slurries with flow behaviors unlike that Saltstone has not been demonstrated. In addition, managing and returning bleed water containing admixtures back to the process is not recommended if satisfactory results can be achieved without admixtures.

The bleed water results for the recommended Clean Cap mix was a function of mixing conditions and time at which bleed water was measured. This is illustrated in Figure 5-1. Consequently, operational flexibility is required to adjust the recommended Clean Cap mix proportions for the new processing equipment and actual conditions in the vault.

The HRWR admixtures were very effective in deflocculating the solid particles (producing slurries in which the solid particles were highly dispersed). The improved dispersion prevented the flocculated particles from trapping some of the mixing water and making it unavailable as the carrier fluid. The result was improved flow properties for any given water to premix ratio compared to slurries without HRWR. If operating experience and technical analysis of the mixing and pumping characteristics of the new facility (mixer capabilities, Saltstone Slurry Hold Tank and peristaltic pump) can accommodate low water, dilatant (deflocculated) slurries improved flow and bleed water characteristics may be achieved.

A summary of the flow behavior and rheological parameters for several clean cap mixes (non Newtonian flow behavior) is provided in Table 5-1. The rheological data were used to calculate engineering parameters for two hypothetical piping conditions intended to represent a simplification of the Z-Area configuration. The hypothetical piping configuration evaluated at two flow rates, 90 and 180 gallons per minute and was defined 1000 feet of 3 inch schedule 80 pipe.

The transitional Reynolds number (between laminar and turbulent flow), the Reynolds number for the flow condition, the flow regime (laminar or turbulent), pressure drop (psi/1000 feet) and apparent viscosity (pipe wall shear stress divided by the pipe wall shear rate) were calculated and provided for comparison purposes of the two types of fluid behavior encountered in this study.

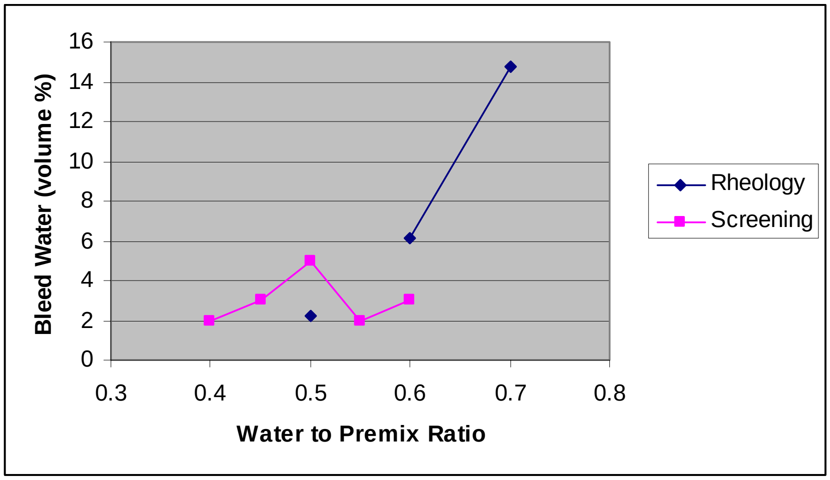


Figure 5-1. Variation in bleed water generated for mixes prepared for rheology and screening experiments.

Table 5-1. Engineering data for Saltstone, the recommended Clean Cap mix, and alternativeClean Cap mix concepts.

	Bingham Plastic		**Power Law**			**90 GPM**				**180 GPM**			
Sample	**η (Pa-sec)**	**τ_{BP} (Pa)**	**K (Pa-sec^n)**	**n**	**$Re_{transition}$**	**RE**	**η_{app} (Pa-sec)**	**Flow Regime**	**ΔP (PSI)/1000 ft**	**RE**	**η_{app} (Pa-sec)**	**Flow Regime**	**ΔP (PSI)/1000ft**
4.5MS1 Reference Saltstone 4.5M Na 10/45/45 cement/slag/fly ash water/premix = 0.60 Mixed in Blender	0.036	8.5	n/a	n/a	5742	4633	0.111	Laminar	38.7	9265	n/c	Turbulent	80.8
4.5MS2 Reference Saltstone 4.5M Na 10/45/45 cement/slag/fly ash water/premix = 0.60 Stirred in Beaker	0.090	8.1	n/a	n/a	3261	1853	0.164	Laminar	56.9	3706	n/c	Turbulent	88.8
SW1 Reference Clean Cap (water) 10/45/45 cement/slag/fly ash water/premix = 0.60 Mixed in Blender	0.025	4.7	n/a	n/a	6013	6671	0.071	Turbulent	24.7	13342	n/c	Turbulent	76.9
SW2 Reference Clean Cap (water) 10/45/45 cement/slag/fly ash water/premix = 0.60 Stirred in Beaker	0.056	7.4	n/a	n/a	4136	2978	0.123	Laminar	42.7	5956	n/c	Turbulent	74.4
SW5 Reference Clean Cap (water) 10/45/45 cement/slag/fly ash water/premix = 0.50 Mixed in Blender	0.152	18.4	n/a	n/a	3088	1097	0.319	Laminar	110.8	2194	0.236	Laminar	164.2
SW6 Reference Clean Cap (water) 10/45/45 cement/slag/fly ash water/premix = 0.50 Stirred in Beaker	0.053	11.5	n/a	n/a	4915	3147	0.155	Laminar	54.0	6293	n/c	Turbulent	83.2
Mix 34 10/45/45 cement/slag/fly ash water/premix = 0.30 Mixed in Blender Adva 540 = 1g	n/a	n/a	0.00121	2.052	1180	974	0.171	Laminar	59.5	940	0.355	Laminar	246.6
Mix 38 10/45/45 cement/slag/fly ash water/premix = 0.30 Mixed in Blender Sika 2100 = 1g	n/a	n/a	0.00350	1.763	1432	1310	0.127	Laminar	44.2	1544	n/c	Turbulent?	n/c
Mix 48 10/45/45 cement/slag/fly ash water/premix = 0.30 Stirred in Beaker Sika 2100 1g	n/a	n/a	0.0012	2.144	1099	638	0.262	Laminar	90.7	577	0.578	Laminar	401.5

Table 5-2 continured. Engineering data for Saltstone, the recommended Clean Cap mix, and alternativeClean Cap mix concepts.

	Bingham Plastic		Power Law			90 GPM				180 GPM			
Sample	**η (Pa-sec)**	**τ_{BP} (Pa)**	**K (Pa-sec^n)**	**n**	**$Re_{transition}$**	**RE**	**η_{app} (Pa-sec)**	**Flow Regime**	**ΔP (PSI)/1000 ft**	**RE**	**η_{app} (Pa-sec)**	**Flow Regime**	**ΔP (PSI)/1000ft**
Mix 76 20/10/70 cement/slag/fly ash Mix 104 water/premix = 0.50 Mixed in Blender	0.0392	4.63	n/a	n/a	4458	4254	0.081	Laminar	28.3	8509	n/c	Turbulent	71.1
Mix 76 20/10/70 cement/slag/fly ash Mix 103 water/premix = 0.40 Mixed in Blender	0.1115	18.5	n/a	n/a	3620	1496	0.278	Laminar	96.5	2991	0.196	Laminar	136.2
Mix 105 30/0/70 cement/slag/fly ash water/premix = 0.50 Mixed in Blender	0.0374	4.11	n/a	n/a	4424	4459	n/c	Turbulent	26.1	8918	n/c	Turbulent	70.2

6.0 Conclusions

Saltstone processed to date can be characterized as a yield pseudoplastic slurry in which the solids are flocculated and which undergoes irreversible reactions over a time. The target water to premix ratio for Saltstone is 0.60. However, several batches of salt solution have required higher water to premix ratios (up to 0.68) to achieve processible slurries that flowed in the vaults. Processing experience with lower water to premix ratios (down to 0.478) is limited to previous attempts to produce and place cold cap slurries.

The current Saltstone slurry was designed to take advantage of the higher water demand required for flocculated particles compared to dispersed particles. A higher water demand corresponds to a higher waste loading since the waste is an aqueous salt solution. Systems based on this concept must be monitored closely because many processing and environmental factors affect the dispersion of the solid particles including shear, humidity, ionic strength of the carrier fluid, etc. (The slurry properties are also affected by the shapes, densities, size distributions of the particles and density of the carrier fluid.)

The approach to designing a Clean Cap formulation was to identify a water to premix ratio that produced a slurry with properties similar to Saltstone using the Saltstone premix composition. In addition, formulation options for the Clean Cap were investigated that may offer advantages, such as, less bleed water and/or less heat generation. However most of the options are outside the operating experience of the Saltstone facility because they require less water and will be more difficult to mix. (Mixing problems were encountered in low water laboratory samples prepared in a blender.) They may also have dilatant rather than pseudoplastic flow behavior which is again outside the operating experience of the Saltstone facility. (A dilatant slurry may flow better in the vault than a pseudoplastic slurry.)

A Clean Cap slurry formulation is recommended based on the testing performed in this study. This mix has slurry properties similar to those of the Reference Saltstone formulation. It contains the same premix ingredients and proportions and displays the same type of flow behavior as the Saltstone formulation. This Clean Cap premix contains 10 wt% cement, 45 wt% slag and 45 wt% fly ash and the resulting slurry prepared with water from the domestic water supply has a maximum water to premix ratio of 0.60 by weight.

Both Saltstone and the recommended Clean Cap slurry can be characterized as yield-pseudoplastic that is irreversible over a time interval that depends on shear rate. In other words the slurry is shear thinning but thickens with decreasing shear and increasing time. The apparent viscosities, yield stresses, and specific gravities (1.6 to 1.7) for the Saltstone slurry and the recommended Clean Cap slurry are similar. However, in laboratory testing, the recommended Clean Cap mix expressed 3 to 6 volume percent bleed water depending on the mixing conditions and the time period the slurry was sheared. Three to six volume percent is more bleed water than that observed for Saltstone slurries and is due to the more rapid settling of solid premix particles in water (specific gravity of 1) compared to salt solution (specific gravity of 1.1 to 1.2).

In an attempt to reduce the bleed water in the Clean Cap mix design, mixes were designed with lower water to premix ratios over the range of 0.3 to 0.5. Dispersants were required to deflocculate the particles to achieve flow at the lower water to premix ratios. (Flocculated particles trap water which is therefore not available as part of the fluidizing media. Deflocculated particles release trapped water which then is available to respond to the shear and to wet the particles.)

High range water reducing, Type F admixtures (carboxyalted polymers from two different manufacturers dosed at 0.02 wt % of the premix) were tested and found to be successful in reducing the water to premix ratio of the reference Clean Cap mix to as low as 0.30. Mixes prepared with water to premix ratios between 0.3 and 0.5 were very flowable in the laboratory tests and displayed minimal bleed water. However, the lower water to premix formulations, less than 0.35, were dilatant rather than pseudoplastic.

The specific gravities for the low water slurries ranged between 1.97 and 1.99 which is an improvement over the Reference Clean Cap with respect to shielding calculations. Unfortunately, these mixes were difficult to mix in the laboratory blender and therefore low water to premix formulations require further testing in to determine whether they are suitable for processing in the Saltstone facility.

Other types of concrete admixtures were also tested but did not produce improvements over the recommended Clean Cap mix (water to premix of 0.60) or the deflocculated Clean Cap mix (reference premix ingredients, water to premix of 0.30 to 0.35 plus HRWR). One exception was an air entraining admixture. The resulting air bubbles improved flow by suspending/propping up the premix particles which counteracted settling. The addition of surfactants to the hold tank may, however, be problematic and therefore can not be recommended without further testing.

Alternative “No Slag” or “Low Slag” premix formulations also offer some advantages over the recommended Clean Cap mix design. However, lower heat and lower materials cost may be off set by higher amounts of bleed water at water to premix ratios required to achieve mixing, pumping and flow in the vault. If testing indicates that formulations with water to premix ratios less than 0.37 can be successfully processed in the new Saltstone facility, the “No Slag” and “Low Slag” Clean Cap formulations should be reconsidered.

Properties of Clean Cap slurries tested in this study are summarized in Table 6-1.

Table 6-1. Summary of Clean Cap slurry properties.

Properties/Engineering Parameters	**Clean Cap Mix Options**		
	Water/Premix **0.60 or higher**	**Water/Premix** **0.40 to 0.50**	**Water/Premix** **0.30 to 0.35**
Formulation	Saltstone and Recommended Clean Cap Mix	Previous Clean Cap formulation (poor flow in vault) and reference premix with HRWR Low-heat, no/low slag premix slurries (0.40)	Low heat, low water to premix slurries containing HRWRs to deflocculate solids
Flow Behavior	Yield Pseudoplastic	Yield Pseudoplastic	Dilatant
Admixture Organic Chemical Addition	No	No	Yes HRWR
Solid Particles	Flocculated High Solids	Flocculated Very High Solids	Deflocculated, Very High Solids
Mixability	Demonstrated	Demonstrated w/premix of 0.478 (previous Clean Caps) and higher	Questionable Not Demonstrated
Pumpability	Turbulent Flow Demonstrated	Turbulent Flow Demonstrated w/premix of 0.478 (previous Clean Caps) and higher	Expected to be: Laminar Flow Reduced Flow Rate Not Demonstrated
Flow in Vault	Acceptable but Improvement Needed Demonstrated	Not Acceptable Failed at w/premix of 0.478 (previous Clean Caps) May be acceptable for low heat/low slag premixes	Expected to be Better than Salstone Not Demonstrated
Bleed Water	Low to Moderate for Reference Clean Cap Mix, Function of conditions in the vault	Low to Moderate Non for w/premix of 0.478 (previous Clean Caps) Higher for low heat/low slag premixes than for Saltstone premix.	Minimal (Less than 3 vol. %)

Shading indicates recommended Clean Cap mix design.

7.0 RECOMMENDATIONS

The recommended Clean Cap formulation for a water to premix ratio of 0.60 is provided below:

Ingredient	Weight Percent	
Premix	62.5	
Cement		6.250
Slag		28.125
Fly Ash		28.125
Water	37.5	

This formulation should be evaluated during run-in of the new Saltstone Facility over a range of water to premix ratios to correlate field performance with properties measured in the laboratory. This mix was designed to closely match the current Saltstone flow behavior and rheologic properties. However it has the potential to generate more bleed water because the carrier fluid has a lower specific gravity than salt solution (1 compared to 1.1 to 1.2) and because it develops gel structure over a slightly longer time, 45 minutes versus 30 minutes which allows for more settling.

Flexibility to adjust the water to premix ratio to overcome the variability in ambient conditions and the conditions of the surface onto which the clean cap is placed should be incorporated into the Saltstone operating procedures. Ambient temperature and humidity and temperature, moisture content, porosity, salt concentration, roughness, slope of the surface onto which the Clean Cap is place affect flow. Set retarders may be required if for some reason the mixing water contains dilute concentrations of salts that result in accelerated set.

If water to premix ratios below 0.40 can be processed in the new Z-Area facility, alternative premix compositions should be considered. These mixes have a higher specific gravity for shielding purposes, generate less bleed water, and may flow better once in the vault. In addition, the no slag or low slag clean cap mixes will be less expensive than the reference premix.

Procedures for evaluating the Z-Area slurries should be reviewed and updated for the modified process and operating conditions. The properties of the Clean Cap slurry produced in Z-Area should be correlated with rheological properties measured in the laboratory in order to develop operating ranges for the process and to predict processibility from laboratory measurements.

8.0 QUALITY ASSURANCE

Calibrated equipment and test instruments were used to perform the work described in this report. The program was performed in accordance with the SRNL Conduct of Research and Development Manual and results were recorded in SRS Laboratory Notebook WSRC-NB-2001-00233.

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