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Cement Free Grout Processing Improvements – 23516

Hannah Hunter
Savannah River Mission Completion, Aiken, SC

ABSTRACT

Radioactive startup of the Saltstone Production Facility (SPF) was authorized by the Department of Energy (DOE) in 1990. In 1998, operations at the Saltstone facility were suspended while seeking alternative processes to prepare the waste that would be processed at Saltstone. Processing was restarted in 2002. The SPF processes low-activity liquid waste and stabilizes it by combining it with dry materials to form a cementitious waste form known as saltstone. Saltstone slurry is formed at the SPF by combining decontaminated salt solution received from Tank 50H via an interarea transfer line with a blend of dry feeds (henceforth referred to as premix). The previous formulation used 45 weight percent (wt%) Grade 120 blast furnace slag (BFS), 45 wt% Class F fly ash (FA), and 10 wt% Type I/II ordinary Portland cement (OPC). The new cement-free formulation is 60 wt% BFS and 40 wt% FA. The liquid and solid components are mixed at a water-to-premix (w/pm) mass ratio of 0.6. The slurry is pumped to enclosed concrete structures, known as Saltstone Disposal Units (SDUs). Within the SDUs the slurry cures to form the non-hazardous, low permeability saltstone waste form. This waste form encapsulates and retains the salt waste contaminants and, thereby, reduces their rate of transport to the surrounding environment.

Beginning in 2012, a multi-phase cement-free feasibility study was performed to determine if there existed a cement-free grout formulation that would have comparable properties to the previously utilized 45/45/10 formulation. The lab work determined that there would be slight changes in some of the properties of the cement-free grout, but these changes were not anticipated to dramatically impact processing. The cement-free formulation (60 wt % BFS, 40 wt% FA), has a lower viscosity and a lower yield stress, and so is slightly easier to mix and pump. The densities of the two formulations are comparable. The cement-free formulation exhibited a shorter gel time, an increased bleed water yield, and an increased heat of hydration compared to the previous formulation during lab testing.

From a processing standpoint, the elimination of the cement component from the premix formulation is advantageous as it allows for more efficient utilization of the dry feed silos. SPF uses four large silos to store the premix feed materials. Under the previous formulation (BFS/FA/OPC), each dry material had its own dedicated silo, and the fourth silo was used as a spare. By going cement-free, the facility can utilize a dedicated silo and a spare silo for each material (BFS/FA). This simplifies procurement, transport, off-loading, and premix materials storage increasing the overall storage capacity for the individual components. This configuration provides greater reliability and approximately doubles the continuous processing potential based on the dry feed storage capacity. This process improvement supports increased salt solution processing throughput due to the new Salt Waste Production Facility (SWPF).

Cement-free processing began in July 2021. The processing data from the first year of cement-free processing has been compared with the previous processing data to evaluate the impacts of switching to the new formulation. Observed parameter changes with cement-free processing include a grout line pressure decrease (13%), while grout flow rate and density were not significantly impacted (a 3% increase and a 2% decrease, respectively). Accounting for the time of year, no significant changes in temperature trends in the representative SDU was observed. To accommodate the expected increase in bleed-water, an aggressive drain-water processing schedule was implemented.

INTRODUCTION

SPF is the facility responsible for processing decontaminated salt solution (DSS), a form of low-level radioactive waste (LLW) at the Savannah River Site (SRS). Saltstone is a cementitious waste form utilized for the stabilization of this waste. Historically, the saltstone slurry was formed by combining the DSS with a blend of dry materials comprised of 45 weight percent (wt%) Grade 100 or 120 blast furnace slag (BFS), 45 wt% Class F fly ash (FA), and 10 wt% Type I/II ordinary Portland cement (OPC); this formulation will be referred to as the 45/45/10 formulation throughout the rest of this paper. The liquid feed and the dry feed are combined at a water-to-premix ratio (wpm) of approximately 0.60 (equivalent to a salt solution-to-premix ratio of approximately 0.85) [1]. The slurry, referred to as "grout," is then pumped to Saltstone Disposal Units (SDUs), enclosed concrete structures where the grout cures to form the non-hazardous, low permeability saltstone waste form [1]. This waste form is capable of encapsulating and retaining the salt waste contaminants [1].

The use of cementitious materials for the immobilization and disposal of LLW in general has been studied throughout the DOE complex since the 1960s [1]. The 45/45/10 formulation was developed to meet the contaminant leaching limits for non-hazardous wastes as set forth in the South Carolina Department of Health and Environmental Control (SCDHEC) Regulation R. 61-79.261.24(b) [1]. Broadly, the cement component in the formulation reacts with water to form a calcium silicate hydrate (CSH) gel that binds particulates together [1]. BFS and FA do not readily react with water, but they can be activated by the calcium hydroxide formed during cement hydration [1]. The BFS in this formulation is the most chemically active component with respect to the retention of the key radionuclides contained in the DSS (namely, Tc-99). The FA reduces the viscosity of the grout, improving pumpability, and acts as a moderator for the heat of hydration produced during the curing of the grout [1].

The DSS is very alkaline, with a typical pH >13. Although they do not react with water, BFS and to a much lesser extent FA, may be activated by the alkaline salt solution to form a gel similar to the CSH gel produced by the hydration of cement [2]. Since the activation of BFS in this instance is not dependent on the calcium hydroxide produced during the cement hydration, the necessity of the cement component for this application was considered. The primary concern was that the elimination of the cement component would reduce the reactivity of the saltstone mixture and in turn adversely impact other grout and saltstone properties. The concern was that a reduced reactivity could lead to prolonged gel times which, in turn, could cause an increase in the development of bleed water on top of the grout within the SDU. Another concern was that if reactivity was reduced, there might be an adverse impact to the physical integrity of the cured saltstone decreasing its capacity to retain the encapsulated contaminants.

From a production perspective, the elimination of the cement component is advantageous as it allows for more efficient utilization of the dry feed silos. SPF currently has four large silos used for the storage of the premix feed materials. Under the 45/45/10 formulation, one silo was utilized for each material with the fourth silo being used as a spare. Under a cement-free formulation, two silos can be allocated for each material, effectively ensuring a spare silo for each, and approximately doubling continuous processing potential based on the dry feed storage capacity.

In 2012, the Savannah River Site began actively supporting research on the viability of a cement-free saltstone formulation [1]. The multiphase study evaluated grout properties in a range of formulations. The properties of interest were those that were thought likely to impact the processing of grout at SPF, the pumping of grout to the SDUs, and the long-term properties of saltstone associated with contaminant retention capacity. As a result of this study, a cement-free formulation (60 wt% BFS, 40 wt % FA) was identified that exhibits comparable fresh and cured grout properties to the 45/45/10 formulation. However, as the determined 60/40 formulation contains a higher percentage of reactive material, the cement-free formulation was expected to have a higher heat generation. This is a property of concern as higher reaction heats could result in higher grout temperatures within the SDUs leading to greater volatilization of organic compounds contained within the original salt waste [1]. Thus, in addition to examining fresh properties such as density, gel time, viscosity, etc. the original down-select report used to determine a suitable cement-free formulation also evaluated if filling an SDU with cement-free grout would challenge temperature limits.

DISCUSSION

The multiphase study to determine the viability of a cement free formulation was conducted in six phases. Phases 1, 2A, 2B, and 3 focused on identifying a viable cement-free formulation by modifying various factors such as BFS wt% and reactivity, FA wt% and reactivity, DSS alkalinity, wpm, etc. This work was conducted by the Vitreous State Laboratory (VSL) from 2012 to 2015. VSL is an institution based within the Catholic University of America and is a leader in glass (vitreous state) science. The fresh properties of the resulting simulated grout samples were then examined and compared with the control formulation (45/45/10). Freshly prepared simulant grouts were tested with respect to gel time, yield stress and viscosity, bleed water generation, heat of hydration, and initial and final setting times. Compressive strength was evaluated using cured grouts. All samples were prepared with dry material grades and vendors used at or comparable to materials used at SPF.

The later phases 4, 5, and 6 focused on developing a thermal model to predict grout temperature trends in the SDU and on obtaining long-term heat generation data, specific heat capacity, and thermal conductivity of the two formulations (45/45/10 and 60/40) to aid in developing said model. The initial model was developed by Atkins in 2017. Atkins is a respected design, engineering, and project management consultancy. The work to empirically measure key thermal properties of the two grout formulations to input into the model was conducted by the Savannah River Ecology Laboratory (SREL) in 2018. Utilization of these parameters in an updated thermal model was performed by the Savannah River National Laboratory (SRNL).

Down-Selecting Report Results

The work done by VSL to arrive at a cement-free formulation that would produce grout comparable to the 45/45/10 formulation determined that the 60/40 BFS/FA formulation would provide a product with similar fresh and cured properties. Phase 1 efforts determined the viability of a cement-free formulation while Phases 2A, 2B, and 3 focused on optimizing the formulation and determining which factors impacted grout properties the most.

Phase 2A indicated that the hydroxide concentration had a significant impact on gel and set times and bleed water generation., with a reduction in hydroxide concentration correlating with a significant increase in both gel time, set time, and bleed water generation. It was also determined during Phase 2A testing, that increasing FA reactivity (by utilizing FA with higher CaO content) had marginal benefits to the SHC of the cured grout but the benefits were not significant enough to warrant further investigation.

Phase 2B further examined the impact of salt solution alkalinity on the fresh and cured properties of the cement-free formulation. This phase investigated if changes to the % BFS utilized or to the wpm could mitigate the adverse impact of reduced hydroxide concentration on gel and set times and bleed water generation. To determine a relevant range of hydroxide concentrations, data was taken from the salt solution waste samples from 2009 to 2013. This provided mean, minimum, and maximum concentrations for the major salt solution components. It was anticipated based on previous testing, that the free hydroxide concentration would be the most impactful component of the major salt solution constituents [1]. Based on the compositional data, a range of hydroxide concentrations were selected for testing while the mean value for the other major salt solution components was utilized. The BFS and FA utilized during this phase of testing were the materials traditionally used at SPF in the production of saltstone.

From the data generated during this phase of testing, it was determined that, broadly, bleed water content and gel and set times decreased with decreasing wpm, increasing hydroxide concentration, and increasing BFS wt % [1]. Yield stress and viscosity were found to decrease with increasing wpm, decreasing hydroxide concentration, and decreasing BFS wt % [1]. It was determined that although decreasing the wpm had a positive impact on the bleed water content, it was preferable to focus on the increased BFS % to mitigate the bleed water content. A decrease in wpm would reduce the proportion of salt solution processed per mass of premix material which in turn would increase the final SDU space needed to process the salt solution inventory at SRS. Another cured property of interest was the Saturated Hydraulic Conductivity (SHC). SHC is the material property that defines how easily a specific fluid may flow through a saturated porous material. A higher SHC would imply faster water transport into the saltstone monolith and faster contaminant transport from the monolith to the surrounding environment.

Phase 3 testing was used to determine a final, viable cement-free formulation. This phase also tested the impact of the other salt solution components. It was found that of these, only aluminum impacted the grout properties significantly, with increased aluminum concentrations leading to higher bleed water content [1]. It was also found that increasing the reactivity of the BFS utilized also reduced bleed water content. Curing profile tests were done on the top two candidate formulations and the 45/45/10 formulation to assess the potential impacts of elevated temperature curing in the SDUs [1]. The results indicated that curing temperatures in the range of 50 to 70 °C had no significant impacts on the cured properties of the grout [1]. The results of the testing to determine relevant comparative fresh and cured grout properties are given in TABLE I below.

TABLE I Summary of Fresh and Cured Properties from Phase 3 Testing

Formulation		Fresh Properties						Cured Properties	
Mix	BFS Grade	Gel time s	Set time s	Yield Stress Pa	Viscosity cP	Bleed %	Density g/cm^3	12-day Heat of Hydration J/g	28-day SHC cm/s
45/45/10	100	3,360	46,800	9.5	86.5	0.7	1.728	83	2.0E-09
60/40	120	2,160	72,000	7.3	58.1	1.2	1.743	125.4	2.0E-09

Based on the results of testing, it was determined that the 60/40 cement-free formulation was the best candidate moving forward. It was noted that the cement-free formulation exhibited greater heat generation. This motivated the thermal modelling work done in the subsequent phases. The initial model developed by Atkins and utilized in Phase 4 performed well in approximately the general temperature trends within the SDU, but in many cases, the model overestimated the peak temperature by 5 to 10 °C [1]. The models used in this phase also exhibited more rapid cooling during non-pouring windows [1]. It was determined that the models' inconsistencies could be partially attributed to a lack of thermal property data for saltstone. Model development was halted until such thermal property data could be obtained (Phase 5). Modelling was revisited in Phase 6 and utilized the thermal property data obtained in Phase 5. Despite the use of updated thermal data, the model continued to give conservative estimates for peak grout temperatures and to indicate more rapid cooling of the grout in comparison to the actual data. But on the basis that the model overestimates the peak temperature, it was thought to be conservative for use in predicting potential temperature profiles in cement-free grout curing in the SDUs. In addition, the model is considered conservative because it does not take into account heat transfer via convection in the SDU vapor space and utilizes an aggressive grout pouring schedule [1]. When modelled with a more realistic pour schedule, the results show that the grout and vapor space temperatures, even with the conservative model, fall within the temperature limits specified in the Documented Safety Analysis (DSA) for SPF.

Process Data from First Year of Cement-Free Grout Processing

Based on the lab work performed for the initial down-select report and the follow-up report, the minor changes in the fresh properties of the cement-free grout (compared to the standard 45/45/10 formulation) were not anticipated to have significant processing impacts [3]. The cement-free formulation produces grout with a lower viscosity and a lower yield stress, so the mixture was expected to be easier to mix and pump. The fresh densities of the cement-free and standard formulations were not expected to be significantly different. The primary areas of concern were the shorter gel time (36 minutes compared to 56 minutes), the increased bleed water content (1.2-1.4 % compared to 0.7 %), and the increased heat of hydration for the cement-free formulation. The reduced gel time of the cement-free formulation is not anticipated to pose an issue during normal processing but may require expedited responses to prevent grout solidifying in the mixer and other portions of the process line if there are process upsets.

The first cement-free grout processing run was conducted on July 22, 2021. Cement-free grout was processed for the next four days. During August 2021, the facility transitioned to the cement-free formulation and by September 2021, all process runs utilized the cement-free formulation. Based on the cement-free down select report results, selected processing variables (grout line pressure, grout density, etc.) were monitored using process monitoring software at SPF. The data for these processing variables was collected for processing runs done with the cement free formulation and compared with process data from a processing run performed with the 45/45/10 grout. The summary of that data is shown in TABLE II below. The 45/45/10 processing data was taken from July 2020 through to the final 45/45/10 process run in August 2021. The cement-free processing data was taken from the first processing run in September 2021 after the transition to cement-free was complete, through to March 11, 2022. After March 11, 2022, grout was poured to a different SDU. To limit the differences between the two data sets, only run data from grout processing to SDU 6 was considered. As predicted, there was a reduction in the grout line pressure, attributed to the lower yield stress and viscosity of the cement-free grout while other variables displayed little change compared to the 45/45/10 formulation.

TABLE II Comparison of Processing Value Averages

	45/45/10	**60/40**	**Difference in Processing Average**
Grout Line Specific Gravity	1.79	1.76	-1.83%
Grout Line Pressure (kPa)	1,028.49	894.39	-13.04%
Grout Line Flowrate (L/s) (**gpm**)	8.55 (**135.57**)	8.81 (**139.59**)	2.97%
Grout Pump Speed (rpm)	11.83	11.73	-0.85%
Grout Pump Current (amps)	41.33	37.83	-8.51%
Grout Hopper Agitator Speed (rpm)	54.98	54.93	-0.08%
Grout Hopper Agitator Current (amps)	2.97	2.93	-1.34%
Premix Screw Feeder speed (rpm)	21.40	21.86	2.18%
Mixer Power (kW)	6.42	6.59	2.65%
Mixer Speed (rpm)	236.89	236.84	-0.02%

As noted, one concern in switching to the cement-free formulation was the higher heat of hydration. The concern was that the higher heat of hydration would generate excess heat within the emplaced saltstone. This could produce higher grout temperatures and potentially impact grout quality and the volatilization of flammable components in the material. Long-term monitoring would be required to accurately represent the temperature profile of the cement free grout. The current first year processing data utilizing the cement-free formulation, accounting for the time of year, does not appear to show any significant changes in temperature trends (Fig. 1 and Fig. 2). This comparison only looked at SDU 6 temperature trends. SDU 6 is a Mega SDU with a capacity of approximately 132,489.4 m^3 (35 million gallons). For a given production rate, due to the larger SDU size, the grout poured to these Mega SDUs may spread more, resulting in thinner layers. This may mitigate excessive temperatures in curing saltstone.

Another long-term property of concern was the increase in bleed water produced by the cement-free grout. Excess bleed water is problematic as it must be drained and ultimately reprocessed through the Saltstone Production Facility. Initial visual observation did not indicate an obvious increase in bleed water, but long-term monitoring will be necessary to get an accurate representation of this processing impact. To preemptively address this concern, SPF has adapted an aggressive drainwater return schedule.

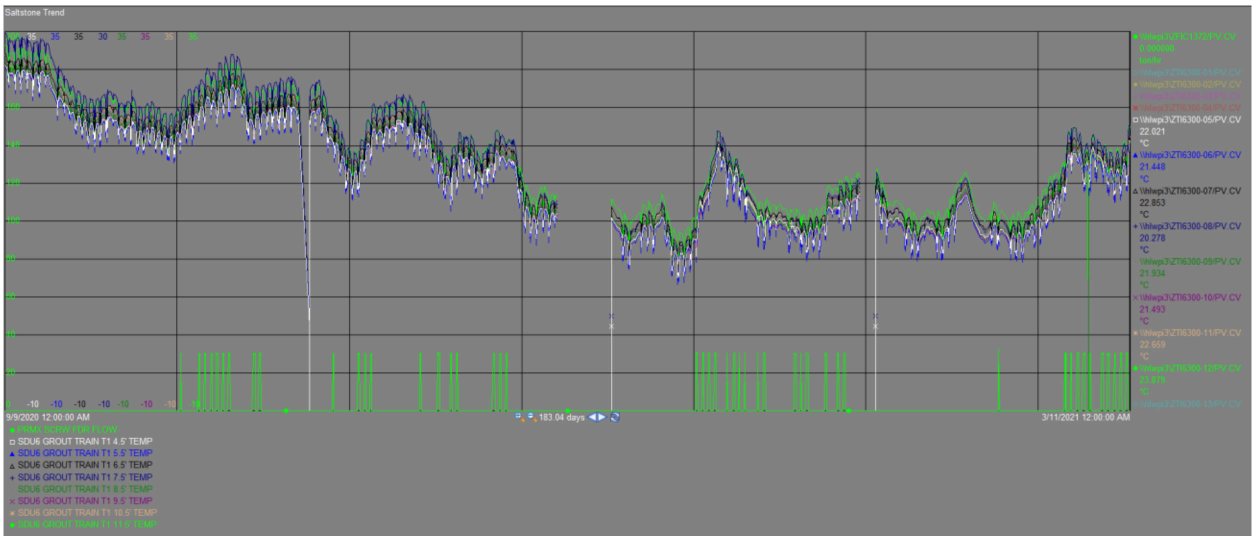

Fig. 1 45/45/10 Temperature Readings for 9/9/2020 through 3/11/2021

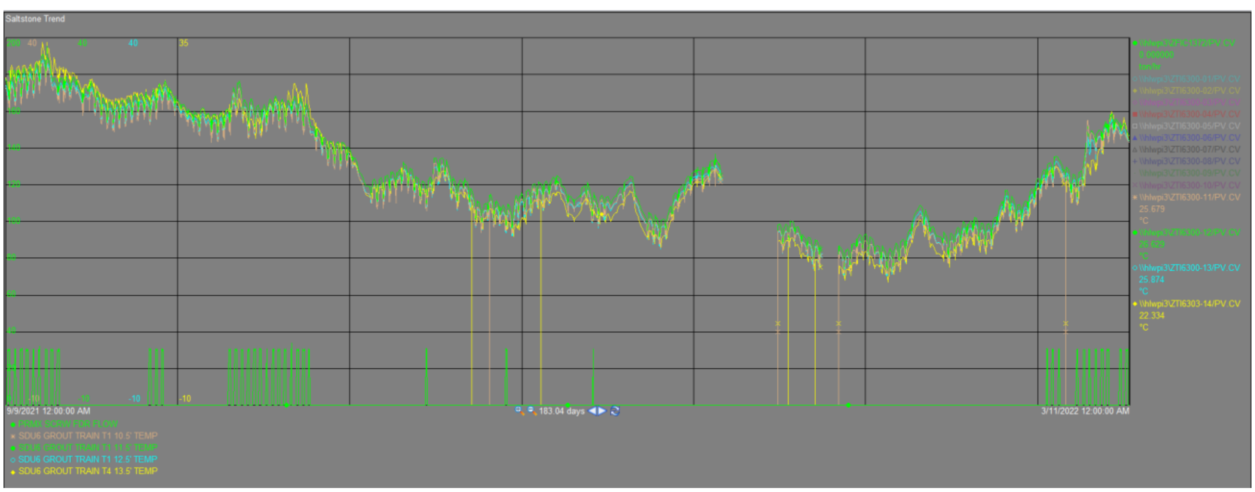

Fig. 2 60/40 Temperature Readings for 9/9/2021 through 3/11/2022

CONCLUSION

The data from the first year of processing with cement-free grout show that initial processing outcomes are consistent with the predictions based on the initial cement-free down select report. Although long-term monitoring is still needed for both the grout monolith temperature and the bleed water content, this transition represents a concrete process improvement. This transition to cement-free processing has enabled SPF to better utilize the storage space in the dry feed silos, effectively doubling the processing potential when based only on dry material inventory.

REFERENCES

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