Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

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Analysis of Tank 30H (HTF-30-19-33, -34), Tank 32H (HTF-32-19-35, -36), and Tank 37H (HTF-37-19-53, -54) Samples for Support of the Evaporator Feed Qualification and Corrosion Control Programs for the 3H-Evaporator

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August 2019

SRNL-STI-2019-00366, Rev. 1

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Prepared for
U.S. Department of Energy

SRNL-STI-2019-00366
Revision 1

Keywords: *3H Evaporator System Supernate Analysis, Radionuclides*

Retention: *Permanent*

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EXECUTIVE SUMMARY

SRNL analyzed samples from Tank 30H, Tank 32H, and Tank 37H to support the Evaporator Feed Qualification and Corrosion Control Programs for the 3H-Evaporator system. The six samples from Tanks 30H, 32H, and 37H all contain highly concentrated salt solutions with sodium concentrations ranging from 13.8 M to 16.9 M. Hydroxide is the dominant anion in all of the samples followed by nitrate and nitrite. The preponderance of the analytical determinations (density, anions, cations) on all three tanks show slightly higher concentrations of solute in the sub-surface sample than in the surface sample, indicating some stratification within the tanks. With the exception of the Tank 30H VDS, all of the samples are somewhat more concentrated compared with the compositions of the previous samples.

The sum of the major cations versus the sum of the major anions show a difference of <5% for all of the samples indicating good data quality for the non-radioactive analytes in the table. The silicon concentrations measured in the VDS and surface samples from Tank 30H, Tank 32H, and Tank 37H were all below detection.

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LIST OF ABBREVIATIONS

AD	Analytical Development
DI	de-ionized
CCP	Corrosion Control Program
EFQ	Evaporator Feed Qualification
IC	ion chromatography
ICP-ES	Inductively Coupled Plasma Emission Spectroscopy
NAS	sodium aluminosilicate
%RSD	percent relative standard deviation
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
TIC	total inorganic carbon
VDS	variable depth sample

1.0 Introduction

Feed limits have been established for the 3H-Evaporator system to ensure nuclear criticality is not possible by preventing the accumulation of sodium aluminosilicate (NAS) solids in the evaporator and that corrosion is minimized. These limits are protected by the Evaporator Feed Qualification Program (EFQ) and the Corrosion Control Program (CCP) that require periodic sampling and analysis to confirm that the waste supernate composition stays within the limits.[1,2]

Savannah River Remediation (SRR) obtained samples from two different heights within each of the three waste tanks supporting the 3H-Evaporator operations on April 24, 2019. The Tank 30H (evaporator drop tank), Tank 32H (evaporator feed tank), and Tank 37H (alternate evaporator drop tank) samples were received by the Savannah River National Laboratory (SRNL) Shielded Cells on the same day. A second set of samples were obtained from Tank 37H on May 10, 2019 to replace the April samples from that tank. The analysis of these samples provides information necessary for determining compliance with the EFQ and CCP. The sample characterization was requested via a Technical Assistance Request.[3]

2.0 Experimental Procedure

The 3H-Evaporator samples from Tanks 30H, 32H, and 37H (used only the May samples from Tank 37H) were opened in the SRNL Shielded Cells and poured into clear plastic beakers. The beakers were photographed, and the masses of the samples determined. Table 2-1 provides the measured mass, volume estimates, and a description of each of the six samples. Figures 2-1, 2-2, and 2-3 show photographs of each set of samples in clear beakers. Figure 2-4 shows all the tank samples together in poly bottles. All of the samples contained the white crystalline solids that were clearly precipitated salts based on observations during the transfer of the samples from the clear beakers to the poly storage bottles. No indication of any dark colored solids was observed in any of the samples.

All six samples received the analyses required by the EFQ that includes determination of Cs-137 by gamma spectroscopy and inductively coupled plasma-emission spectroscopy (ICP-ES) to determine Na, Al, Si, and other metals. All six samples also received the analyses required by the CCP. The CCP analysis suite includes determination of free hydroxide and ion chromatography (IC). The total inorganic carbon (TIC) was also determined on the surface samples to provide a concentration for the carbonate anion present in the samples.

Density measurements were made on well-mixed (unfiltered) aliquots of the samples using calibrated volumetric tubes at ambient cell temperature (29 °C).

For the CCP analysis, de-ionized (DI) water dilutions were made in triplicate from a well-mixed (unfiltered) sample and submitted to Analytical Development (AD) for analysis. A blank of the DI water was also prepared along with the samples. The water dilutions were analyzed by ion chromatography, total inorganic carbon, and free hydroxide methods.

Triplicate aliquots of the well-mixed (unfiltered) sample from each sample receiving the EFQ analysis suite were prepared for analysis using the warm acid strike method[4] A reagent blank and three silicon standard solutions were submitted for analysis with the samples. The samples prepared by warm acid strike were submitted to AD for analysis by ICP-ES and gamma spectroscopy. The ICP-ES analysis was conducted by F/H Lab due to the failure of the AD instrument.

Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in Manual E7, Procedure 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2. This review meets the acceptable criteria to comply with the TAR requesting this work. Data are recorded in the electronic laboratory notebook system as notebook/experiment number Y7081-00081-32.

Table 2-1. Sampling Description and Mass of the Tank 30H, 32H, and 37H Samples

Tank	Sample ID	Sample Type	Sample Mass (g)	Estimated Sample Volume (mL)	Estimated Solids Volume (mL)	Description
Tank 30H	HTF-30-19-33	Surface	96.37	~60	~20	Dark tinted solution with white crystalline solids
Tank 30H	HTF-30-19-34	VDS	331.8	~205	~50	Dark tinted solution with white crystalline solids
Tank 32H	HTF-32-19-35	Surface	73.62	~50	~5	Dark tinted solution with white crystalline solids
Tank 32H	HTF-32-19-36	VDS	233.4	~155	~90	Dark tinted solution with white crystalline solids
Tank 37H	HTF-37-19-53	Surface	120.5	~80	~20	Dark tinted solution with white crystalline solids
Tank 37H	HTF-37-19-54	VDS	328.0	~200	~150	Dark tinted solution with white crystalline solids

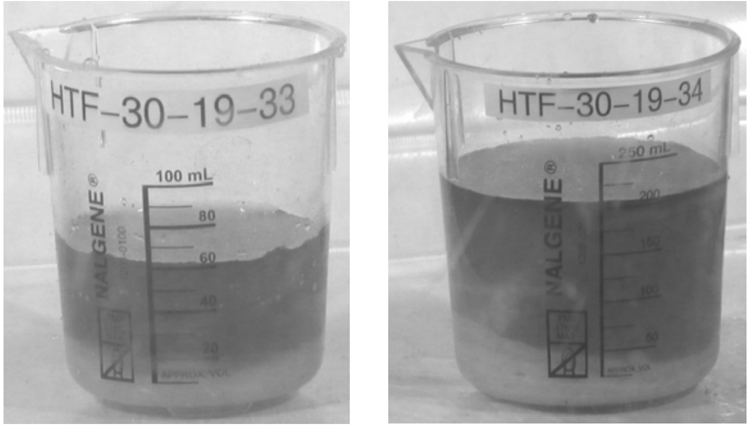

Figure 2-1. 3H-Evaporator Samples from Tanks 30H

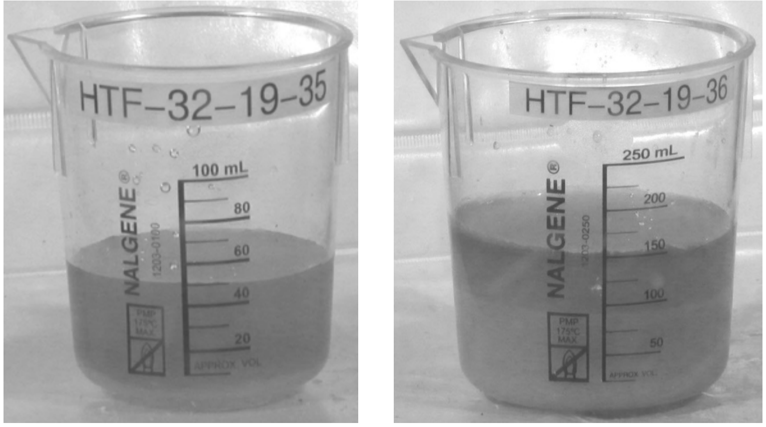

Figure 2-2. 3H-Evaporator Samples from Tanks 32H

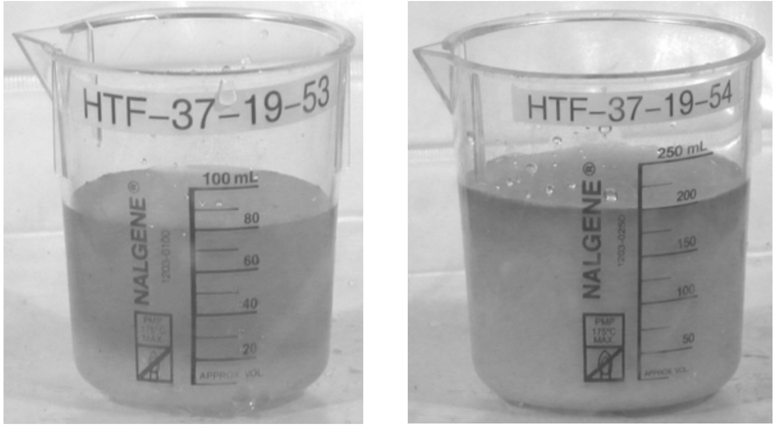

Figure 2-3. 3H-Evaporator Samples from Tanks 37H

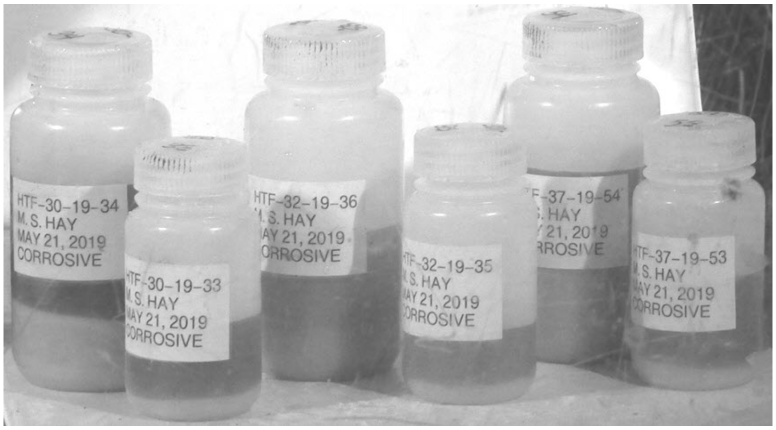

Figure 2-4. View of the 3H-Evaporator Samples

3.0 Results and Discussion

The following tables contain the results from the analysis of the samples. The tables show the average concentrations and the percent relative standard deviations (RSD) for the triplicate sample preparations. Results preceded by "<" indicate the analyte was below the limits of quantification for all three replicate aliquots of the sample. Results preceded by "≤" indicate that at least one of the replicates for the sample was above the limits of quantification while one or more of the replicates analyzed were below detection. The percent RSD presented in the table only includes the uncertainty associated with sub-sampling/sample preparation in the Shielded Cells and the analytical method. The estimated one sigma percent uncertainty provides an indication of the uncertainty associated with the analytical method as reported by AD. Neither of these measures of uncertainty includes the uncertainty associated with sampling a large waste tank. Previous investigations indicate the uncertainty from taking a small sample from a large waste tank can be significant.[5,6,7]

The results in Table 3-1 for the two samples from Tank 30H show both samples to be highly concentrated salt solutions with a sodium concentration of 14.5 M in the surface sample and 15.7 M in the VDS. Hydroxide is the main anionic species in both solutions with a concentration of 9.46 M in the surface sample and 9.92 M in the VDS. The other main anions in the two solutions are nitrate and nitrite. The nitrate values show an RSD of 20% for both Tank 30H samples. This may result from sub-sampling difficulties due to the presence of crystallized salts in the sample, some of which is likely sodium nitrate. Inclusion of more or less of these solids during each sub-sampling event to obtain the three replicates could lead to the higher uncertainty in the nitrate concentration. The aluminum, chromium and phosphorus from the ICP-ES analysis of the surface sample show very large RSD's and these values should be used with caution. The composition of the VDS from Tank 30H is generally slightly more concentrated than the surface sample indicating some stratification in the tank. The surface sample from Tank 30H is slightly more concentrated than the previous surface sample while the VDS shows a similar composition to the previous sample.[8] The sum of the major cations versus the sum of the major anions shows a difference of <5% for each of the two Tank 30H samples providing an indication of good data quality.

The results for the two samples from Tank 32H in Table 3-1 indicate some stratification throughout the tank depth profile. The sodium concentration measured in the Tank 32H VDS of 15.3 M is higher than the 13.8 M sodium concentration measured in the surface sample. As with Tank 30H samples, the anionic constituent with the highest concentration is hydroxide followed by nitrite and nitrate. The sum of the major cations versus the sum of the major anions indicates good data quality with a difference of <5% for each of the two Tank 32H samples. The surface sample from Tank 32H is more concentrated than the previous surface sample mainly due to a large increase in the sodium hydroxide concentration. The VDS is also more concentrated than the previous VDS.[8]

In the results from the two samples from Tank 37H in Table 3-1, the VDS sample shows higher concentrations for most of the major components of the samples than found in the surface sample. Much higher concentrations for sodium and carbonate account for most of the difference between the surface sample and the VDS. Sodium is the dominant cation with a concentration of 14.0 M in the Tank 37H surface sample and 16.9 M in the VDS. The nitrate and phosphate from the IC analysis show an RSD of >20% for the Tank 37H surface sample. As discussed previously with the Tank 30H samples, this may result from sub-sampling difficulties due to the presence of crystallized salts in the sample. The aluminum, chromium and phosphorus from the ICP-ES analysis of the Tank 37H VDS show very large RSD's and these values should be used with caution. Again, the sum of the major cations versus the sum of the major anions indicates good data quality with a difference of <5% for each of the two Tank 37H samples. Both the surface sample and the VDS from Tank 37H show higher concentrations for most species than measured in the previous sample.[8]

The high carbonate concentration measured in the Tank 37H VDS prompted a request to measure the carbonate concentration in the decanted supernate of the sample excluding any crystallized solids. Table 3-2 provides the results from the analysis of samples of the decanted supernate analyzed by AD. A much lower carbonate concentration of 0.056 M was measured versus the 1.86 M measured in the total sample. This appears to indicate that much of the carbonate in the total sample resides in the crystallized solids. Given that the solubility of sodium carbonate would be expected to decrease slightly with a rise in temperature, it's unlikely all the sodium carbonate solids in the Tank 37 VDS were dissolved in the salt solution at the warmer tank temperatures. The carbonate solids were likely picked up during the sampling event from the surface of the salt cake.

All of the silicon concentrations measured in the VDS and surface samples from Tank 30H, Tank 32H and Tank 37H were below detection. The standards used for the silicon analysis (50 mg/L silicon in the solution prepared by warm acid strike to final concentrations of 0.5, 1.0, and 2.0 mg/L) were all close to the target concentrations with differences from the targeted concentrations of 3-16%. The silicon concentration was below detectable levels in the process blank.

Table 3-1. ECP, CCP, and other Analytical Data for Tank 30H, 32H and 37H Samples. (Averages and %RSD values are of triplicate measurements)

analyte	method	units	est. 1σ	HTF-30-19-33		HTF-30-19-34		HTF-32-19-35		HTF-32-19-36	
				average	RSD	average	RSD	average	RSD	average	RSD
sample type	--	--	--	surface		vds		surface		vds	
density @ 29°C	grav.	g/mL	5%	1.56	0.3%	1.59	0.7%	1.49	0.3%	1.54	0.1%
Cs-137	gamma scan	dpm/mL	5%	4.21E+09	4.2%	3.65E+09	4.1%	3.13E+09	3.4%	3.10E+09	0.6%
Ba-137m				3.98E+09		3.45E+09		2.96E+09		2.93E+09	
OH^-_{free}	titration	M	10%	9.46E+00	6.9%	9.92E+00	4.0%	7.98E+00	5.3%	7.79E+00	3.5%
F^-	IC	M	10%	<2.71E-02	--	<2.86E-02	--	<2.66E-02	--	<2.37E-02	--
CHO_2^-	IC	M	10%	<1.14E-02	--	<1.21E-02	--	<1.12E-02	--	<1.00E-02	--
Cl^-	IC	M	10%	2.41E-02	4.1%	2.58E-02	3.3%	2.05E-02	1.2%	1.97E-02	2.9%
NO_2^-	IC	M	10%	2.50E+00	10%	2.18E+00	11%	2.43E+00	1.6%	2.49E+00	1.1%
NO_3^-	IC	M	10%	2.22E+00	20%	1.95E+00	20%	1.87E+00	1.8%	2.40E+00	12%
PO_4^{3-}	IC	M	10%	1.15E-02	4.4%	1.28E-02	12%	<5.32E-03	--	6.44E-03	16%
SO_4^{2-}	IC	M	10%	<5.35E-03	--	<5.66E-03	--	<5.26E-03	--	9.41E-02	19%
$C_2O_4^{2-}$	IC	M	10%	<5.84E-03	--	<6.18E-03	--	<5.74E-03	--	<5.12E-03	--
Br^-	IC	M	10%	<3.22E-02	--	<3.40E-02	--	<3.16E-02	--	<2.82E-02	--
CO_3^{2-}	TIC	M	10%	9.44E-02	3.9%	7.98E-02	9.5%	1.03E-01	3.6%	5.28E-01	23%
Al	ICP-ES	mg/L	10%	7.90E+03	120%	2.25E+04	11%	2.31E+04	0.6%	1.84E+04	4.6%
		M		2.93E-01		8.33E-01		8.56E-01		6.83E-01	
B	ICP-ES	mg/L	10%	3.60E+02	1.6%	3.27E+02	3.7%	2.87E+02	2.9%	2.82E+02	2.2%
Ca	ICP-ES	mg/L	10%	<2.39E+01	--	<2.41E+01	--	<2.28E+01	--	<2.34E+01	--
Cr	ICP-ES	mg/L	10%	1.09E+02	117%	3.10E+02	17%	3.39E+02	3.5%	2.68E+02	12%
Fe	ICP-ES	mg/L	10%	<2.39E+01	--	2.70E+01[a]	2.1%	3.05E+01	4.3%	2.55E+01[a]	5.6%
Li	ICP-ES	mg/L	10%	<2.39E+01	--	<2.41E+01	--	<2.28E+01	--	<2.34E+01	--
Na	ICP-ES	mg/L	10%	3.34E+05	3.5%	3.61E+05	2.3%	3.17E+05	1.9%	3.51E+05	5.3%
		M		1.45E+01		1.57E+01		1.38E+01		1.53E+01	
P	ICP-ES	mg/L	10%	1.49E+02[a]	112%	3.83E+02	33%	4.27E+02	4.1%	3.12E+02	43%
Si	ICP-ES	mg/L	10%	<2.66E+01	--	<2.68E+01	--	<2.55E+01	--	<2.61E+01	--
Zn	ICP-ES	mg/L	10%	2.65E+01	9.3%	2.64E+01	3.5%	2.40E+01[a]	2.6%	2.42E+01	1.5%
Anions	sum	M	--	1.47E+01	--	1.51E+01	--	1.34E+01	--	1.46E+01	--
Cations	sum	M	--	1.45E+01	--	1.57E+01	--	1.38E+01	--	1.53E+01	--

est.1σ = estimated one sigma percent uncertainty as reported by AD.

a = only two replicates above detection were used to calculate the average and RSD

Table 3-1. ECP, CCP, and other Analytical Data for Tank 30H, 32H and 37H Samples. (Averages and %RSD values are of triplicate measurements) Continued

analyte	method	units	est. 1σ	HTF-37-19-53 average	RSD	HTF-37-19-54 average	RSD
sample type	--	--	--	surface		vds	
density @ 29°C	grav.	g/mL	5%	1.52	0.6%	1.65	2.3%
Cs-137	gamma scan	dpm/mL	5%	3.53E+09	6.9%	3.17E+09	6.6%
Ba-137m				3.34E+09		3.00E+09	
OH^{-}_{free}	titration	M	10%	8.72E+00	1.6%	7.91E+00	3.4%
F^{-}	IC	M	10%	<2.60E-02	--	<2.90E-02	--
CHO_2^{-}	IC	M	10%	<1.10E-02	--	<1.22E-02	--
Cl^{-}	IC	M	10%	2.29E-02	4.1%	2.09E-02	1.4%
NO_2^{-}	IC	M	10%	2.58E+00	7.7%	2.65E+00	3.2%
NO_3^{-}	IC	M	10%	1.88E+00	21%	2.81E+00	2.8%
PO_4^{3-}	IC	M	10%	7.10E-03	27%	1.10E-02	3.5%
SO_4^{2-}	IC	M	10%	<5.15E-03	--	1.01E-01	5.4%
$C_2O_4^{2-}$	IC	M	10%	<5.62E-03	--	<6.26E-03	--
Br^{-}	IC	M	10%	<2.30E-02	--	<6.90E-03	--
CO_3^{2-}	TIC	M	10%	8.60E-02	3.7%	1.86E+00	5.3%
Al	ICP-ES	mg/L	10%	2.19E+04	3.7%	8.20E+03	161%
		M		8.11E-01		3.04E-01	
B	ICP-ES	mg/L	10%	3.12E+02	6.8%	2.81E+02	11%
Ca	ICP-ES	mg/L	10%	<2.30E+01	--	<2.50E+01	--
Cr	ICP-ES	mg/L	10%	3.25E+02	7.8%	1.70E+02	96%
Fe	ICP-ES	mg/L	10%	2.48E+01	4.9%	≤2.56E+01	--
Li	ICP-ES	mg/L	10%	<2.30E+01	--	<2.50E+01	--
Na	ICP-ES	mg/L	10%	3.23E+05	6.4%	3.88E+05	5.4%
		M		1.40E+01		1.69E+01	
P	ICP-ES	mg/L	10%	3.84E+02	29%	3.44E+02[a]	126%
Si	ICP-ES	mg/L	10%	<2.56E+01	--	<2.78E+01	--
Zn	ICP-ES	mg/L	10%	2.70E+01[a]	6.0%	<2.50E+01	--
Anions	sum	M	--	1.42E+01	--	1.76E+01	--
Cations	sum	M	--	1.40E+01	--	1.69E+01	--

est.1σ = estimated one sigma percent uncertainty as reported by AD.

a = only two replicates above detection were used to calculate the average and RSD

Table 3-2. Tank 37H Variable Depth Sample Carbonate Ion Concentration in the Total Sample and in the Decanted Supernate

Tank 37H VDS (HTF-37-19-54)	**Average CO_3^{2-} (M)**	**RSD**
Decanted Supernate (excluding crystallized solids)	0.056	3.8%
Total Sample (including crystallized solids)	1.86	5.3%

4.0 Conclusions

The six samples from Tanks 30H, 32H, and 37H all contain highly concentrated salt solutions with sodium concentrations ranging from 13.8 M to 16.9 M. Hydroxide is the dominant anion in all of the samples followed by nitrate and nitrite. The preponderance of the analytical determinations (density, anions, cations) on all three tanks show slightly higher concentrations of solute in the sub-surface sample than in the surface sample, indicating some stratification within the tanks. With the exception of the Tank 30H VDS, all of the samples are somewhat more concentrated compared with the compositions of the previous samples.

The sum of the major cations versus the sum of the major anions show a difference of <5% for all of the samples indicating good data quality for the non-radioactive analytes in the table. The silicon concentrations measured in the VDS and surface samples from Tank 30H, Tank 32H, and Tank 37H were all below detection.

5.0 Acknowledgements

The contributions of Dee Wheeler and Monica Jenkins, in preparing the samples, and those of Amy Ekechukwu, Mark Jones, Nathan Wyeth, John Young, and Tom White, for providing analytical services, are appreciated and acknowledged.

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