Operational Management of Chromium Recycling From Tannery Wastewater

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***Abstract*— *Operational management is an important step in production process of a chemical reaction for getting good quality of yield with economical way as taken in recycling of chromium from tannery waste. It is most widely used the Chromium (III) salts as a chemicalin the process of tanning. Only 60%-70% of chromium salt is used to reacts with theskins and hides but 30%-40% of remaining chromium chemicals are wasted in form of the solid and liquid (as a tanning solutions). Consequently, the recoveryand recycling of the chromium metal content of existed wastewaters is essential for economic reasons and environmental protection. Recycling and recovery of chromium metal is supported by using chemical precipitation methods. For achieving this special aim, calcium hydroxide plus alum and magnesium oxide are used as two precipitating agents. This is a confirmatory Study on the effects of stirring time, pH, sludge and settling rate volume in batch experiments. These Results are showed that the optimum pH for efficient recovery was done at 8.5, good sludge with high settling rate and lower volume during recovery process was achieved. Based on these findings an economical recovery plant was designed. The recovery achieved about 99(%) at pH 8 with stirring at 90 rmp.*

Keyword*— Economical Recovery, Chromium, Tanning, Chemicals, Recycling.

I. INTRODUCTION

Today, thepeople of whole world are facing three main environmental issues as increasing environmental pollution, food shortage and human population. The first one is observing a serious issue in the under developing countries.Developing countries also have their share for their increased rate of uncontrolled discharge of waste into environment due to rapid industrialization. It is known as major leather production centers in the world as Brazil, Mexico, Japan, China, South Korea, Pakistan and India [1].

Pakistan’s leather industry is one of the major sources of foreign exchange. At present about 90 % of the leather is exported in finished form. During the year 2004-06 export earnings from leather and leather goods amounted to US $ 745 million. About 54 million skins and hides were processed during this year [2].

According to a survey report conducted by National Engineering Services Pakistan that in Pakistan, there are about 595 tanneries but most of them situated in groups or industrial regions in Lahore, Karachi, Kasur, Multan, Faisalabad, Peshawar, Sialkot and Gujranwala. traditional tanneries as small and medium-scale units still succeed, but there are some large well-mechanized and export oriented tanneries are situated in Karachi.

leather and leather-based product industry needs some raw material which is drawn from a livestock’scontainingthe 36.7 million sheep, 19.5 million buffaloes, 21.5 million cattle, 5.5million horses and 49.5 million goats which areproducing about 75 million of goat and sheep skins and over 18.6 million of cattle hides per year in Pakistan [3].

Tanning is one of the oldest and fastest growing industries in Pakistan. The various processes involved in leather tannery generate wastes in solid and liquid form containing substantial quantities of chromium along with organic matter, lime and sulfide. These wastes need to be treated and made suitable for disposal. Thus tannery waste management has gained a paramount significance in Pakistan and elsewhere in the world [4]. Chromium is one of the most hazardous waste materials emitted from tanneries. Frequent studies and researches have struggled to define the intracellular status of chromium as carcinogen or mutagen for its chemical nature, ultimately. It is reported in literature that Cr (III) species can be mutagenic and genotoxic inside the cell. The ability of Cr (III) to participate in non-enzymatic phosphorylation and crosslink DNA and proteins as influence calcium transport channels has been reported[5]. It is ionized of reaction sites for chrome tanning with the carboxyl groups on side chains of the collagen protein.

The potential of toxicity of some forms of chromium are not serious if chromium waste water is treated effectively on regular basis. Sometimes its concentration is abnormally high but is discharged as an effluent[5].

The objective of this paper is managing chemical process during recycling of chromium from waste for waste management.

II. MATERIAL AND METHOD

Wastewater Sampling

Samples were taken from different tanneries during the working hours of during continuing industrial processes. Wastewater (composite samples) before finishing process was collected in pre-washed plastic containers from the tanneries on Lahore-Sheikhupura road. The tanneries sampled were: Hafeez Shafi Tanneries (Pvt) Ltd, Lahore.

Sample transportation: The stoppers closing the sample containers were fixed in place by adhesive (PVC) tap to prevent leakage. The samples were transported securely without damaging the container or seal.

Storage: The samples were stored in a cool (less than 30ºC) and dry place.

Chemical Analysis

The analyses were carried out by using standard ASTM methods as follows. Reagent grade chemicals were used in all tests[6].

Determination of chromium[7]

Summary of test method: Hexavalent chromium reacts with 1,5-diphenylcarbohydrazide (s-diphenylcarbozide) in an acid medium to produce a reddish-purple color. The intensity of the color formed is proportional to the hexavalent chromium concentration.

Apparatus: Spectrophotometer (UV-1700 Shimadzu) equipped with a cell having a path length of 10 mm.

Reagents: Chromium stock solution (1 mL ≡ 0.10 mg Cr): Potassium dichromate (0.2828 g), that has been oven dried at 105°C for 1 h, was dissolved in distilled water to make 1 L.

Standard solution (1 mL ≡ 0.001 mg Cr): Ten mL of chromium stock solution was diluted to 1 L with distilled water.

Calculation:

The hexavalent chromium concentration was calculated as follows:

$$Cr^{+6}\ (g\ L^{-1}) = (W_S - W_B)\ (50/S)$$

Where:

W_S = Chromium found in the sample, mg L^{-1}

W_B L^{-1} = Chromium found in the sample blank, mg

S = Volume of sample used, mL

Determination of hardness[8]

test method Summary: Magnesium and Calcium ions in water are appropriated by the adding of disodium ethylenediamine tetra acetate. The end point of the reaction is detected by means of Chrome Black T[4], which has a red color in the presence of calcium and magnesium.

Regents: Ammonium hydroxide solution (1 + 4): One volume of NH_4OH (sp gr 0.90) was mixed with 4 volumes of water.

Calcium indicator — Hydroxynaphthol blue.

Hardness indicator solution — Chrome Black T[3] (0.5 g) was dissolved in 50 mL of diethanolamine or triethanolamine and stored the solution in a dark-colored bottle. This solution had a storage life of several months.

Procedure: High hardness — The clear sample (50 mL) was transferred into a clear colorless container utilizing a white background. The pH of the sample was adjusted to 7-10 by adding NH_4OH solution or HC1 solution. To this was added 0.5 mL of buffer solution and 2 drops of indicator solution and the mixture was stirred. The standard Na_2H_2EDTA solution was added slowly from a burette with continuous stirring until the color changed from red to blue. The titration was completed within 5 min after the buffer addition. If the titration required more than 20 mL of the titration solution, the sample was diluted and the test was repeatd.

Low hardness — The low-hardness (0.5 to 5.0 mg L^{-1} as $CaCO_3$) was determined as above by using 100 mL sample and titrating by means of a micro-burette. The quantity of the reagents used was twice than used above(Brown SJ, 2010).

Determination of biological oxygen demand (BOD) [9]

Reagents: Standard sodium thiosulphate (0.25N) — . Two mg of the salt was dissolved in 100 ml of distilled water in conical flask and a few drops of concentrated H_2SO_4 + 20 mL standard IO_3^- solution were added. The solution was titrated for librated iodine against sodium thiosulphate by shaking the flask until pale straw yellow color appeared. After this a few drops of starch solution was added until color changed from blue to colorless).

Dissolved 2 g starch powder + 0.2 g salicylic acid as a preservative in 100 ml boiled distilled water.

Procedure: A dilution water was prepared by aerating the required volume of distilled water in a container by bubbling compressed air to attain saturation. To this was added 1 mL each of phosphate buffer, $MgSO_4$, $CaCl_2$, $FeCl_3$ solutions for each liter of dilution water.

The BOD bottle was filled to its half with dilution water. A suitable volume of sample (20-40 mL) was transferred to the BOD bottle. After this the bottle was filled to its full capacity with dilution water and stopped immediately. A blank was prepared using plain dilution water. One sample bottle was kept for initial dissolved oxygen (DO) and the other bottle was incubated at 20ºC for 5 days.

Determination of chemical oxygen demand (COD) [10]

Apparatus: Spectrophotometer (UV-1700 Shimadzu), heating block (capable of maintaining a temperature of 165 ±2°C throughout); COD tubes (borosilicate glass, 16 by 100 mm with TFE-fluorocarbon-lined screw caps); laboratory blender; vacuum pretreatment device (consisting of vacuum chamber connected to a pump assembly that draws sample through the chloride removal agent; an internal gauge on the vacuum chamber must be utilized to indicate a vacuum level of generating and displaying a vacuum of 508-635 mm of mercury); mixing vials (borosilicate, 20-30mL capacity, with TFE-fluorocarbon-lined screw closures).

Reagents: Chloride removal agent — Sodium bismuthate ($NaBiO_3$) in an inert medium, packaged in single-used cartridges. Manganese III COD reagen t— Pre-measured COD tubes of reagent and catalyst. Reagent is stabilized by complexation in sulfuric acid solution where there are several possible manganese III complexes. The predominant species in 1N H_2SO_4 are $Mn_2(SO_4)_3$ and two hydrated species, $[Mn(H_2O)_5HSO_4]^{2+}$ and $[Mn(H_2O)_5(HSO_4)_2]^+$. Potassium acid phthalate standard solution (1 mL ≡ 1 mg COD) — 0.851 g of dried (120°C, overnight) potassium acid phthalate ($KC_8H_5O_4$) primary standard dissolved in distilled water to make 1 L. Sulfuric acid — (H_2SO_4) concentrated, reagent grade (sp gr 1.84). The photometric cell was filled with reagent water, the prepared sample for COD and measurements were made against the reagent water filled cell at 510 nm. The prepared reagent blank served as a quality control only, and was not used to zero the instrument. The cell was inverted several times prior to reading in order to ensure that the filter disc and any undigested suspended solids do not settle, so that they do not interfere with photometric readings.

Calculation: COD values (mg L^{-1}) were calculated from the calibration curve [11].

Determination of solids[12]

Summary: These tests are based on evaporation of the water sample under standard conditions and weighing the dry residue.

Apparatus: Platinum dish; Gooch crucible; desiccators.

Procedure:

Total solids: The unfiltered thoroughly shaken sample (100 mL) was evaporated to dryness in a pre-weighed platinum dish on a stream or water bath. The residue was dried at 103°C for one hour.

Dissolved solids: The sample was filtered to reduce its turbidity to less than 1 unit. The clear sample (100 mL) was taken in a pre-weighed platinum dish and evaporated to dryness. The residue was dried at 103°C for one hour.

Suspended solids: The water sample (2 L) was filtered through a pre-weighed Gooch crucible having an asbestos mat, dried for one hour at 103°C, cooled in a desiccator to a constant weight.

Calculations and formula:

Total Solids mg L^{-1} = Increase in weight of pt-dish in mg × 10

Total dissolved solids mg L^{-1} = Increase in weight of pt-dish in mg × 10

Suspended solids = Total solids – Dissolved solids.

Recovery Process of chromium from wastewater

The chromium was removed from the wastewater by using CaO + alum and MgO as the precipitating agent. The procedure is given as follows:

Precipitation: All the chemicals used were of analytical reagent grade and obtained from E. Merck. The precipitation of Cr(III) was carried out in two steps. In the first step lime solution along with alum was used then in the second step the residual Cr(III) was precipitated by use of MgO solution. A saturated lime solution was prepared by soaking excess of CaO in distilled water (100 mL). A 10% solution of MgO was prepared by dissolving MgO (10 g) in distilled water (100 mL) in a 250-mL [13].

Optimization of process

The process was optimized and managed by changing pH, amount of alum and amount of chromium present in the sample. By changing these parameters the settling rate was determined by measuring the height of supernatant, sludge volume and chromium in the supernatants by standard methods[14].

For examplesludge volume, settling rate and the shape of the precipitate for all precipitating agents were measured at the pH where fixed at the optimalrate. For the determine sludge volumes and settling rate, samples of wastewater were transferred into graduated cylinders, then sludge volume or height of supernatant was measured after 5 h.

III. RESULTS

Chemical Analysis ofwastewater samples

The results of the analyses of samples are given in Table 1 that shows the chemical variation in waste water due to important tanning process. Tanning process is started with the pickling and mostly commercial chrome tannin reagents are used in powder form as they contain about 25 % of Cr_2O_3. In this process Basic chrome sulphate (BCS) liquors are used. So, table-1 has high values of chromium due high concentration of chromium dissolved in tanning solution.

Liquid waste Water consumption per kg of raw hides varies from tannery to tannery.

Water consumption in tanning process as normal requirement of 50 litre per kg of hides processingbut it is generally found in the tanneries consumes more water than normal requirement. The waste consists of: solid content 3.5-6.5%; volatile matter 20-48%; inorganic matter 51-74%; chromium 0.37-0.75%.

A considerable quantity of sludge is also present in composite wastewater. The settle able matter is responsible for the sludge generation.

Table.1: Chemical Analytical data of samples

Parameter	**Hafeez Shafi Tanneries**	
	Mean	*Range*
pH	4.42	4.0 - 4.8
BOD (mgL^{-1})	1419.8	1079 - 1822
COD (mgL^{-1})	3278.4	2987 - 3698
SO_4^{2-} (mgL^{-1})	619	421 - 735
PO_4^{3-} (mgL^{-1})	472.8	258 - 658
TDS (mgL^{-1})	1437.4	1025 - 1854
TSS (mgL^{-1})	609.8	487 - 698
TS (mgL^{-1})	2337	2045 - 2587
S^{2-} (mgL^{-1})	405.2	256 -547
Cr (mgL^{-1})	3636	3187 - 3987
Phenol (mgL^{-1})	50.6	14 - 98
Ca (mgL^{-1})	381.2	245 - 478
Na (mgL^{-1})	737.8	698 - 874
K (mgL^{-1})	186.2	125 - 269
NH_3 (mgL^{-1})	1764.4	1024 - 3210

Managing the operation as pH and chromium recycling

It is shown in Fig. 1 that at pH 7.0 – 7.5 about 112 – 228 mg L^{-1} chromium was present in the treated effluent which is not acceptable for further treatment.

These results demonstrate that Magnesium Oxide (MgO) is a good and suitable agent for precipitation chemical reaction which is very help full for recovering the chromium metals from tanning waste solution. Below fig. 1 gives the relationship pH and time for recovery of chromium that is important for recovery operation and productions.

In thecases of Magnesium Oxide MgO involving recycling systems have good chance in improving the efficiency and make it more economical for treatment of wastewater.

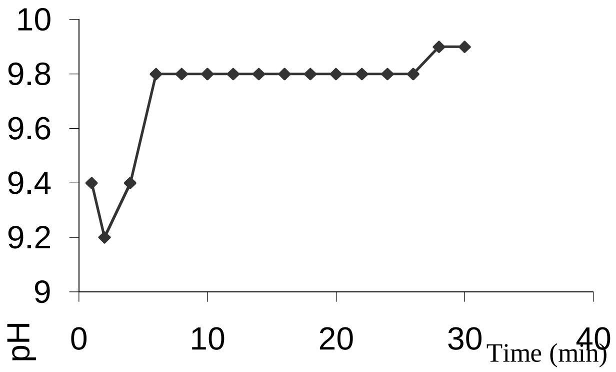

Fig.1: Graph showing change of pH (by use of lime) with time

Constant variation between Chromium concentration and recovery

The wastewater management processes are based on common effluent treatment plants, which involve chromium recovery. the results are shown in Fig. 2. A chromium concentration range varying from 200 to 6000 mg^{-1} was studied under optimum conditions.

The expected concentrationis 6000 mg/L of chromium in wastewater from tanning process which is needed to be recycled. The data indicate that the recovery (%) increase with the chromium content of the sample linearly following the equation $y = 0.0013x + 90.672$with $r^2 = 0.9606$ (Fig. 2)

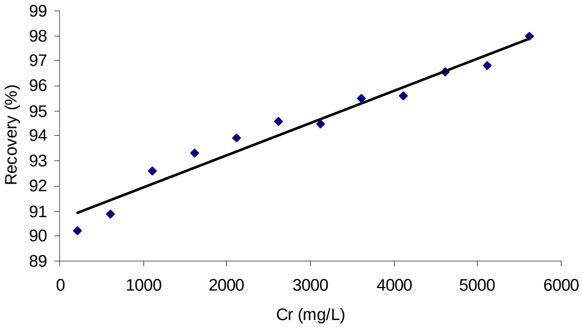

Fig.2: Graph between chromium recovery and concentration

Managing the two variable as time and pH for recycling of Chromium

The recovery of chromium (III) which is closely related variables time and pH. And in this process the use of MgO is most extensive because it is highly ionized molecule.

Because of its good settling rate and high bulk density of matter that present in chromr wastewater.This is a series wise process and gives the benefits for increasing the precent of recovery of chromium during the operation as shown in fig. 3.

Below figure is the best proof for specified the optimum pH increasing with time when use the MgO regent. But commercially MgO available chemicals have important amounts of calcium salts as impurities for chemical coagulation. So, this is very important that good grades of MgO can play a major role for getting economical and high percentage of chrome recovery from wastewater as shown in fig- 3.

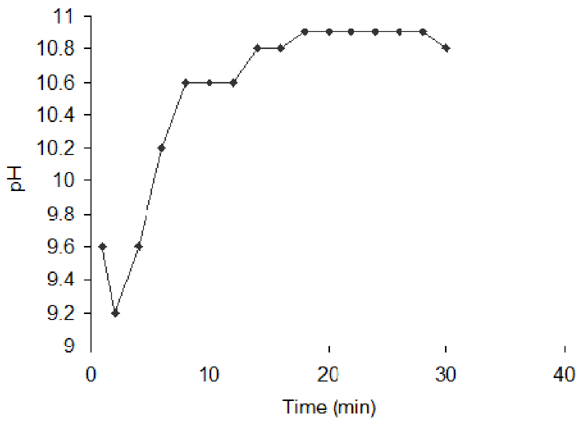

Fig.3: Graph showing change of pH (by use of MgO) with time

IV. DISCUSSION

The reduction of chromium in wastewater is carried out by using the replacing with sulfur dioxide or technical sugars because it has very low molecular weight as compare to chromium metal. The aim of tanning is to make leather more durable and softwith stability as a wide range of bearing the physical and chemical conditions under humidity and pH.Different reports showing that the tanning chemicals are capable for the process of cross-linking among the molecules of collagen protein. This is basically degree of crosslinking needs careful consideration as if cross-linking is too much then harsh and brittle product is obtained. It is clearly seen from the results that when pH increases from acidic to basic the recovery of chromium increases [15].

The environmentin which alkali are used in precipitating of chromium (III) hydroxide can also effect on the settling rate of chromium (III) Sulphatethat characteristics of colloidal chromium (III) hydroxide particles which are closely related with the zeta potential as report in recovery process. But nature of alkali as fectors depend on distribution of particle sizes, degree of aggregation, settling behavior and morphological properties of chromium (III) hydroxide are important consideration [16].

This is a common practice all over the world that using of the chromium (III) sulphate for tanning process for obtaining the soft and flexible leathers and recovery process is needed for everyone. Another solutionof these problems for removing the pollution of chromium containing wastewater are simple remediation of chromium (VI) and and biotechnology treatment processes have been developed previous. Treatement method as Physio-chemical adsorption has long been researchedbut the process cost is much high as compare to chromium recovery treatment method. Bioremediation method of wastewater treatment by strains of bacteria can very effectively degrade chromium (VI) and it is economically favorable but the bactericidal toxicants at many waste sites would be dangerous again for environmental pollution. Chemical reduction of chromium salt is well known to remove chromium (VI) effectively and rapidly. [17].

Chromium chemicals are manufactured in most of the industrial countries of the world. Pakistan imports about 70% of the chromium compounds to be used in tanneries. It is therefore, necessary to develop methods for the industrial production of these compounds and conversion of the waste chromium form tanneries wastewater as re-useable compounds [18].

V. CONCLUSIONS

The research assumptions are based on treatment of waste water containing chromium sulphate from tanning operation. The idea about recovering and recycling process is good and its related achievements have been shown that precipitating method is cheaper and most economical. The operational pH for the precipitating is 8.5 which good for production of Cr sludge with high settling rates.Lower volume is obtained with using MgO as the precipitating agent. Next time researchers needs develop the practical and implementation by using mechanical design models for enhancement for wastewater treatment technology.

REFERENCES

[1] Blankenship JK, CA Langton, JC Musall, and WB Griffin. 2012. New Materials Developed To Meet Regulatory and Technical Requirements Associated with In-situ Decommissioning of Nuclear Reactors and Associated Facilities. SDD-2012-00003, Savannah River Nuclear Solutions, Aiken, South Carolina.

[2] Brown SJ. 2010. “Caustic Side Solvent Extraction At the Savannah River Site: Operating Experience and Lessons Learned – 10105.” In WM2010 Conference Proceedings, March 7–11, 2010, Phoenix, Arizona.

[3] Daniel RC, JM Billing, RL Russell, RW Shimskey, HD Smith, and RA Peterson. “Integrated Pore Blockage-Cake Filtration Model for Crossflow Filtration.” Chemical Engineering Research and Design,vol. 89, no.7, pp.1094–1103, 2011.

[4] Dresel PE, MJ Truex, and K Cantrell. 2008. Remediation of Deep Vadose Zone Radionuclide and Metal Contamination: Status and Issues. PNNL-18114, Pacific Northwest National Laboratory, Richland, Washington.

[5] Dunn K and M Louthan. “Evidence of Corrosive Gas Formed by Radiolysis of Chloride Salts in Plutonium-Bearing Materials.” Journal of Nuclear Materials Management,vol. 38, no. 3, pp. 82,Nov. 2010.

[6] EPA – US Environmental Protection Agency. 2011. Environmental Cleanup Best Management Practices:

[7] Fox KM, DK Peeler, JM Pareizs, CL Crawford, and TB Edwards. 2014. Evaluation of Defense Waste Processing Facility (DWPF) Glass Samples After an Extended Melter Outage. SRNL-STI-2014-00302, Savannah River National Laboratory, Aiken, South Carolina.

[8] Gin S, A Abdelouas, LJ Criscenti, WL Ebert, K Ferrand, T Geisler, MT Harrison, Y Inagaki, S Mitsui, KT Mueller, JC Marra, CG Pantano, EM Pierce, JV Ryan, JM Schofield, CI Steefel, and JD Vienna. “An International Initiative on Long Term Behavior of High Level Nuclear Waste Glass.” Materials Today,vol. 16, no. 6, pp. 243–248, 2013.

[9] Herman D, M Poirier, M Fowley, M Keefer, T Huff, W Greene, and J Gilmour. 2011. “Testing of the Second Generation SpinTek Rotary Filter.” In WM2011 Conference Proceedings, March 7–11, 2011, Phoenix, Arizona.

[10] Hoffman EN, PE Zapp, BJ Wiersma, and TB Edwards. 2010. “Probability-Based Corrosion Control for High Level Waste Tanks.” Presented at CORROSION 2010, March 14–18, 2010, NACE International, San Antonio, Texas.

[11] Jenkins KD, YN Deng, and SL Orcutt. 2012. 2012 WTP Tank Utilization Assessment. 24590-WTP-RPTPE-12-001, Rev. 0, River Protection Project, Hanford Tank Waste Treatment and Immobilization Plant, Richland, Washington.

[12] Kim DS, DK Peeler, and P Hrma. “Effects of Crystallization on the Chemical Durability of Nuclear Waste Glasses,” Ceramic Transactions Series,vol. 61, pp. 177–185, 1995.

[13] Kim D, MJ Schweiger, CP Rodriguez, WC Lepry, JB Lang, JV Crum, JD Vienna, FC Johnson, JC Marra, and DK Peeler. 2011. Formulation and Characterization of Waste Glasses with Varying Processing Temperature. PNNL-20774 (EMSP-RPT-009), Pacific Northwest National Laboratory, Richland, Washington.

[14] Kim DS, MJ Schweiger, WC Buchmiller, and J Matyas. 2012. Laboratory-Scale Melter for Determination of Melting Rate of Waste Glass Feeds. PNNL-21005, Pacific Northwest National Laboratory, Richland, Washington.

[15] Kim DS and JD Vienna. 2012. Preliminary ILAW Formulation Algorithm Description. 24590-LAWRPT-RT-04-0003, Rev. 1, ORP-56321, River Protection Project, Hanford Tank Waste Treatment and Immobilization Plant, Richland, Washington. Michalske T. July 15, 2014.

[16] Peters TB, MR Poirier, and SD Fink. “Processing Macrobatch 2 at the Savannah River Site Integrated Salt Disposition Process.” Separation Science and Technology,vol. 45, pp. 1801–1806, 2010.

[17] Reed S and J James. 2010. Environmental Restoration Overview - Mountain Creek Industrial Center. Naval Facilities Engineering Command Southeast, Jacksonville, Florida.

[18] Russell RL, JM Billing, HD Smith, and RA Peterson. “Validation of Ultrafilter Performance Model Based on Systematic Simulant Evaluation.” Industrial & Engineering Chemistry Research,vol. 48, no. 22, pp. 10077–10086, 2009.

[19] Schonewill PP, RC Daniel, RR Russell, RW Shimskey, CA Burns, JM Billing, BM Rapko, and RA Peterson. 2012. “Development of an S-Saltcake Simulant Using Crossflow Filtration as a Validation Technique.” Separation Science and Technology, Special Issue: Seventeenth Symposium on Separation Science and Technology for Energy Applications 47(14-15): 2098–2107.

[20] Thomas S and G Dickert. 2013. “Regulatory Framework for Salt Waste Disposal and Tank Closure at the Savannah River Site.” In WM2013 Conference Proceedings, February 24–28, 2013, Phoenix, Arizona.

[21] Thorson M. 2008. Basis of Recommendation for Use of Spherical Resorcinol Formaldehyde Resin as the Primary Cesium Ion Exchange Resin in the WTP. 24590-WTP-RPT-RT-07-005, Bechtel Waste Treatment Plant, Richland, Washington.

[22] Vienna JD, JV Ryan, S Gin, and Y Inagaki. 2013. “Current Understanding and Remaining Challenges in Modeling Long-Term Degradation of Borosilicate Nuclear Waste Glasses.” International Journal of Applied Glass Science,vol. 4, no.4, pp. 283–294,2015.

[23] Vienna JD and DS Kim. 2014. Preliminary IHLW Formulation Algorithm Description. 24590-HLWRPT-RT-05-001, Rev. 1, River Protection Project, Hanford Tank Waste Treatment and Immobilization Plant, Richland,Washington. Weber WJ. “Radiation and Thermal Ageing of Nuclear Waste Glass.” Procedia Materials Science,vol. 7, pp. 237–246, 2014.