Halide, Chromate, and Phosphate Impacts on LAW Glass for Dynamic Flowsheet. 24590-WTP-MCR-PET-09-0037, Rev. 1

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

**P.O. Box 450
Richland, Washington 99352**

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Date

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24590-WTP-MCR-PET-09-0037, Rev 1

 Total No. Pages: 8

Model Change Request (MCR)

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Page 1 of 1

PART 1: REQUEST INITIATION (to be completed by Requester)

Title of Request:		
Halide, Chromate, and Phosphate Impacts on LAW Glass for Dynamic Flowsheet (G2)		
Requester: Rod Gimpel	Phone: 371-3146	Requested Group Assignment: v 6.0
Indicate model to be changed:		
☐ Steady-State (AES) ☒ Dynamic (G2) ☐ OR (Wit) ☐ Lab OR (Wit) ☐ Other ()		
Describe proposed change in Attachment A: Proposed Change Description.		
 Requester Signature	06-04-09 Date	
Irvine Stone Input Checker (Print)	 Signature	6/16/10 Date
Ernest D. Lee Flowsheet and ORP Deliverables Lead (Print)	 Signature	6/25/10 Date

PART 2: REQUEST TRACKING (to be completed by Configuration Management Designee)

Date Submitted to CM: 6-15-10	Actual Model Group Assignment: V6.0
Date Scoping Completed: NA	Date V&V Completed: NA

PART 3: REQUEST SCOPING (to be completed by Modeler)

Estimated Time to Complete Change Request:	Total: 20	Implementation: 4	Run: 16
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PART 4: REQUEST CLOSURE (to be completed by Configuration Management Designee)

Comments:		
Verification and Validation Test Plan Document No.: NA		
Verification and Validation Report Document No.: NA		
Model Design Document No.: NA		
☐ The requested change has been implemented into model version NA		
☐ The MCR is cancelled (provide reference for cancellation in comment section). NA		
☐ The MCR is superseded by Revision NA		
All information has been entered into the Flowsheet/Model Change Request database and the MCR is closed.		
 Modeling CM Designee (Print)	 Signature	6/29/10 Date

Model Change Request (MCR)

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Attachment A: Proposed Change Description

Additional pages may be added to the Proposed Change Description, as necessary. All pages must have the MCR number and be numbered sequentially as Page A-x. Enter N/A in any sections that are not applicable.

Facility (indicate all facilities impacted by proposed change):

☐ Pretreatment
 ☒ LAW Vitrification
 ☐ HLW Vitrification
 ☐ Balance of Facilities
 ☐ Lab

System designator(s) (indicate all systems impacted by proposed change):

System Designators and Names

LFP & LAW Melter Feed Process System

Applicable Drawing Numbers and Revisions

24590-LAW-M5-V17T-00001, Rev. 5

Component designator(s) (indicate all components impacted by proposed change):

Equipment Numbers and Names

LAW melter feed preparation vessels (MFPV), LFP-VSL-00001/3

Model Designator

LFP-VSL-00001/3

Parameters (Indicate all parameters impacted by proposed change. Include current design and proposed values. Indicate applicable references.):

Parameter

Halide, Chromate, and Phosphate limits on LAW Glass

Current Design Value

None

Proposed Value

Calculated per Attachment A1

Proposed Change (Describe in sufficient detail so that it may be accurately translated into a model change.):

Revision 1 of this MCR changed Equation 6 in Attachment A1 only.

Melter studies have shown that halide, chromium, and phosphates can cause precipitation of solids that can interfere the melting process. Pilot melter data now shows what concentrations LAW glass can tolerate. These limits shall be incorporated into the existing LAW glass algorithm per Attachment A1.

References (Include justification basis [required].):

CCN-150795, Halide, Chromate, and Phosphate Impacts on LAW Glass Salt Limits

PNNL 18501, Glass Property Data and Models for Estimating High-Level Waste Glass Volume.

Attachment A1

Halide, Chromate, and Phosphate Impacts on LAW Glass - Dynamic Flowsheet (G2)

(Revision 1 changed Equation 6 only.)

Rename M_{glass}^{batch} as $M_{glass.p1}$ in the model's logic. The final glass calculated will again be called M_{glass}^{batch} for calculating the final glass mass and glass formers.

$$M_{glass.p2} = \text{MAX}(M_{glass.p1}, M_{K2O} / 0.05, M_{P2O5} / 0.025) \quad \text{Eq. 1}$$

where: M_{K2O} and M_{P2O5} are the masses of potassium and phosphorous in the waste as the oxide.

Note that CCN 150795 does not give an absolute upper limit for P_2O_5 but HLW studies have limited it to 2.5 wt% per report PNNL 18501, *Glass Property Data and Models for Estimating High-Level Waste Glass Volume*. HLW glasses are limited to 6.5 combined wt% for P_2O_5 and CaO. Since LAW glasses uses significant amounts of CaO as a glass former, this limit will also be observed. Too much CaO and P_2O_5 can lead to a solids precipitate forming on the surface of the molten glass in the melter, which can greatly hinder melter operations.

$$g_{SO3} = M_{SO3} / M_{glass.p2} \quad \text{Eq. 2}$$

where: M_{SO3} is the mass of sulfate in the waste as SO_3 .

$$BC_{Halide} = \text{IF}(g_{SO3} > 0.0059, 0.0022, -2.1111 g_{SO3} + 0.014656) \quad \text{Eq. 3}$$

$$BC_{Cr2O3} = \text{IF}(M_{P2O5} / M_{glass.p2} > 0.02499, 0.0063, \text{IF}(M_{K2O} / M_{glass.p2} \leq 0.00540, 0.0063, 0.008)) \quad \text{Eq. 4}$$

$$M_{glass}^{batch} = (M_{glass.p2}, (M_{Cl} + 0.3M_F) / BC_{Halide}, M_{Cr2O3} / BC_{Cr2O3}) \quad \text{Eq. 5}$$

where: M_{Cl} and M_F are the masses of chlorine and fluorine in the waste.

M_{Cr2O3} is the mass of chromium in the waste as the oxide.

Glass formers are now calculated as before but now using the new M_{glass}^{batch} value. However, the glass former amount A_{CaO} is not determined yet. Rename A_{Cao}^{batch} as A_{CaOX} and A_{SiO2}^{batch} as A_{SiO2X} . The glass is checked to ensure the combined concentration of CaO and P_2O_5 in the glass does not exceed the 6.5 wt% cited above and the A_{CaOX} adjusted accordingly. Therefore:

$$A_{Cao}^{batch} = \text{IF}((A_{CaOX} + M_{CaO} + M_{P2O5}) / M_{glass.p2} > 0.065, 0.065 - (M_{CaO} + M_{P2O5}) / M_{glass.p2}, A_{CaOX} / M_{glass.p2}) \quad \text{Eq. 6}$$

where: M_{CaO} is the mass of calcium in the waste as the oxide.

$$A_{SiO2}^{batch} = A_{SiOX} - (A_{CaO} - A_{CaOX})$$

Flowsheet Output

Please print the following values to the *law-glass-property* print file for validation:

 $M_{\text{glass.p1}}$ $M_{\text{glass.p2}}$ BC_{Halide} BC_{Cr2O3}

Model Change Request (MCR)

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Attachment B: Change Implementation Plans

Additional pages may be added to the Change Implementation Plan, as necessary. Additional Change Implementation Plans may be created using the **Insert | Change Implementation Plan** command. They shall be numbered sequentially and each new one added will supercede all previous Change Implementation Plans in the MCR. All pages must have the MCR number and be numbered sequentially as Page B-x. Enter N/A in any sections that are not applicable.

Change Implementation Plan 1

Model/Current Version: Dynamic (G2) Flowsheet Version 5.0

System Environment: As described in *System Design For Process Modeling*, 24590-WTP-PL-TE-01-008

Required Model Changes:

The implementation is shown in the G2 procedure below:

law-frit-calculation (adj-tank: class mixer-oxide-glass-formers, this-frit-frac: class mineral-array) = (class mineral-array, text)

l, s, ls: class component_array;

m-al2o3, m-b2o3, m-caO, m-cl, m-cr2o3, m-f, m-fe2o3, m-k2o, m-li2o, m-mgo, m-na2o, m-p2o5, m-sio2, m-so3, m-tio2, m-toc, m-total, m-zno, m-zro2, m-glass, m-glass-p1, m-glass-p2: float;

BC-Cr2O3, BC-Halide, c-high-sulfate, c-k2o-na2o, c-transition, d, g-na2o, g-so3, Li-Check, x-na2o: float;

A-Al2O3, A-B2O3, A-CaO, A-CaOX, A-C12H22O11, A-Fe2O3, A-Li2O, A-MgO, A-Na2O, A-SiO2, A-SiOX, A-TiO2, A-ZnO, A-ZrO2: float;

DF-Sulfur: float = law-so4-df-1; {initially 0.16}

DF-Cl: float = the reaction-conversion of cl-vaporization-law;

DF-F: float = the reaction-conversion of f-vaporization-law;

BoraxLAW, BoricAcidLAW, IronOxideLAW, KyaniteLAW, LithiumCarbonateLAW, OlivineLAW, RutileLAW, SilicaLAW, SodaAshLAW, SugarLAW, WollastoniteLAW, ZincOxideLAW, ZirconLAW: float;

glass-property: text;

begin

l = the liquid_components of adj-tank;

s = the solid_components of adj-tank;

ls = the scratch-components of adj-tank;

{Step 1: sum up total waste}

call g2-array-add (l, s, ls);

{Step 2: calculate waste-oxide, kgs}

call inventory-to-oxide-calculation (ls, waste-oxide-law);

m-total = call g2-array-sum (waste-oxide-law);

m-al2o3 = waste-oxide-law[al2o3-ox];

m-b2o3 = waste-oxide-law[b2o3-ox];

m-caO = waste-oxide-law[cao-ox];

m-cl = waste-oxide-law[cl--ox];

m-cr2o3 = waste-oxide-law[cr2o3-ox];

Model Change Request (MCR)

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Required Model Changes:

```

m-f = waste-oxide-law[f--ox];
m-fe2o3 = waste-oxide-law[fe2o3-ox];
m-k2o = waste-oxide-law[k2o-ox];
m-li2o = waste-oxide-law[li2o-ox];
m-mgo = waste-oxide-law[mgo-ox];
m-na2o = waste-oxide-law[na2o-ox];
m-p2o5 = waste-oxide-law[p2o5-ox];
m-sio2 = waste-oxide-law[sio2-ox];
m-so3 = waste-oxide-law[so3-ox];
m-tio2 = waste-oxide-law[tio2-ox];
m-zno = waste-oxide-law[zno-ox];
m-zro2 = waste-oxide-law[zro2-ox];
  
```

{Step 3: calculate m-glass}

```

c-k2o-na2o = 0.215 / (1 + 0.66 * m-k2o / m-na2o);
c-transition = 0.35875 / (1 + 42.5 * m-so3 / m-na2o);
c-high-sulfate = 0.0077 * m-na2o / m-so3;
  
```

```

x-na2o = min (0.21, c-k2o-na2o, c-transition, c-high-sulfate);
g-na2o = min (x-na2o, 0.04 * m-na2o / m-k2o);
m-glass-p1 = m-na2o / g-na2o;
m-glass-p2 = max (m-glass-p1, m-k2o / 0.05, m-p2o5 / 0.025);
g-so3 = m-so3 / m-glass-p2;
  
```

```

if g-so3 > 0.0059
  then
    BC-Halide = 0.0022
  else
    BC-Halide = -2.111 * g-so3 + 0.014656;
  
```

then

BC-Halide = 0.0022

else

BC-Halide = -2.111 * g-so3 + 0.014656;

```

if m-p2o5 / m-glass-p2 > 0.02499
  then
    BC-Cr2O3 = 0.0063
  else
    begin
      if m-k2o / m-glass-p2 <= 0.0054
        then
          BC-Cr2O3 = 0.0063
        else
          BC-Cr2O3 = 0.008;
    end;
  
```

then

BC-Cr2O3 = 0.0063

else

begin

if m-k2o / m-glass-p2 <= 0.0054

then

BC-Cr2O3 = 0.0063

else

BC-Cr2O3 = 0.008;

end;

m-glass = max (m-glass-p2, (m-cl + 0.3 * m-f) / BC-Halide, m-cr2o3 / BC-Cr2O3);

{Step 4: calculate additives}

A-Al2O3 = max (0.061, m-al2o3 / m-glass) * m-glass - m-al2o3;

if A-Al2O3 < 0.0 then A-Al2O3 = 0.0;

A-B2O3 = 0.1 * m-glass - m-b2o3;

if A-B2O3 < 0.0 then A-B2O3 = 0.0;

A-Fe2O3 = max (0.055, m-fe2o3 / m-glass) * m-glass - m-fe2o3;

if A-Fe2O3 < 0.0 then A-Fe2O3 = 0.0;

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Required Model Changes:

$A\text{-TiO}_2 = 0.014 * m\text{-glass} - m\text{-tio}_2$;
 if $A\text{-TiO}_2 < 0.0$ then $A\text{-TiO}_2 = 0.0$;

$A\text{-ZnO} = 0.035 * m\text{-glass} - m\text{-zno}$;
 if $A\text{-ZnO} < 0.0$ then $A\text{-ZnO} = 0.0$;

$A\text{-ZrO}_2 = 0.03 * m\text{-glass} - m\text{-zro}_2$;
 if $A\text{-ZrO}_2 < 0.0$ then $A\text{-ZrO}_2 = 0.0$;

$A\text{-Na}_2\text{O} = \max(0.054, g\text{-na}_2\text{o}) * m\text{-glass} - m\text{-na}_2\text{o}$;
 if $A\text{-Na}_2\text{O} < 0.0$ then $A\text{-Na}_2\text{O} = 0.0$;

$d = 0.66 * m\text{-k}_2\text{o} / m\text{-glass} + \max(0.054, g\text{-na}_2\text{o})$;

$A\text{-CaOX} = (0.015 + 0.055 / (1 + \exp((d - 0.17) / 0.02))) * m\text{-glass} - m\text{-cao}$;

if $((A\text{-CaOX} + m\text{-cao} + m\text{-p}_2\text{o}_5) / m\text{-glass-p}_2) > 0.065$
 then

$A\text{-CaO} = (0.065 - (m\text{-cao} + m\text{-p}_2\text{o}_5) / m\text{-glass-p}_2) * m\text{-glass-p}_2$

else

$A\text{-CaO} = A\text{-CaOX}$;

if $A\text{-CaO} < 0.0$ then $A\text{-CaO} = 0.0$;

$\text{Li-Check} = 1 - ((100 * d - 5.4) / 12.75)^2$;

if $\text{Li-Check} < 0.0$

then

$A\text{-Li}_2\text{O} = 0.0$

else

$A\text{-Li}_2\text{O} = 0.043 * \text{Li-Check}^{0.7} * m\text{-glass} - m\text{-li}_2\text{o}$;

if $A\text{-Li}_2\text{O} < 0.0$ then $A\text{-Li}_2\text{O} = 0.0$;

$A\text{-MgO} = (0.0148 + 0.0149 / (1 + \exp(100 * d - 9))) * m\text{-glass} - m\text{-mgo}$;

if $A\text{-MgO} < 0.0$ then $A\text{-MgO} = 0.0$;

$A\text{-SiOX} = m\text{-glass} - m\text{-total} - A\text{-Al}_2\text{O}_3 - A\text{-B}_2\text{O}_3 - A\text{-CaO} - A\text{-Fe}_2\text{O}_3 - A\text{-Li}_2\text{O} - A\text{-MgO} - A\text{-Na}_2\text{O} - A\text{-TiO}_2 - A\text{-ZnO}$
 $- A\text{-ZrO}_2 + m\text{-so}_3 * (1 - \text{DF-Sulfur}) + m\text{-cl} * (1 - \text{DF-Cl}) + m\text{-f} * (1 - \text{DF-F})$;

$A\text{-SiO}_2 = A\text{-SiOX} - (A\text{-CaO} - A\text{-CaOX})$;

if $A\text{-SiO}_2 < 0.0$ then $A\text{-SiO}_2 = 0.0$;

{Step 5: calculate sucrose, kgs}

$m\text{-toc} = \text{call total-organic-mass (ls)}$;

$A\text{-C}_{12}\text{H}_{22}\text{O}_{11} = ((\text{ls}[\text{nitrate-position}] + \text{ls}[\text{nitrite-position}]) / 16 - m\text{-toc} / 12) * \text{oxide-mws}[\text{sugar-position}]$;

$\text{glass-property} = "A\text{-Al}_2\text{O}_3, [A\text{-Al}_2\text{O}_3], A\text{-B}_2\text{O}_3, [A\text{-B}_2\text{O}_3], A\text{-CaO}, [A\text{-CaO}], A\text{-Fe}_2\text{O}_3, [A\text{-Fe}_2\text{O}_3], A\text{-Li}_2\text{O}, [A\text{-Li}_2\text{O}], A\text{-MgO}, [A\text{-MgO}], A\text{-Na}_2\text{O}, [A\text{-Na}_2\text{O}], A\text{-SiO}_2, [A\text{-SiO}_2], A\text{-TiO}_2, [A\text{-TiO}_2], A\text{-ZnO}, [A\text{-ZnO}], A\text{-ZrO}_2, [A\text{-ZrO}_2], A\text{-C}_{12}\text{H}_{22}\text{O}_{11}, [A\text{-C}_{12}\text{H}_{22}\text{O}_{11}]$

$M\text{-Total}, [m\text{-total}], M\text{-Glass}, [m\text{-glass}], \text{DF-Sulfur}, [\text{DF-Sulfur}], M\text{-Glass-P1}, [m\text{-glass-p1}], M\text{-Glass-P2}, [m\text{-glass-p2}], \text{BC-Halide}, [\text{BC-Halide}], \text{BC-Cr}_2\text{O}_3, [\text{BC-Cr}_2\text{O}_3]"$;

{Impurity Adjustment}

$\text{SilicaLAW} = (A\text{-SiO}_2 - 0.69635 * A\text{-Al}_2\text{O}_3 - 1.06905 * A\text{-CaO} - 0.89374 * A\text{-MgO} - 0.51573 * A\text{-ZrO}_2) * (1 + C\text{-}$

Model Change Request (MCR)

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Required Model Changes:

Moisture);

if SilicaLAW < 0.0 then SilicaLAW = 0.0;

IronOxideLAW = (A-Fe2O3 - 0.15754 * A-MgO) * (1 + C-Moisture);

if IronOxideLAW < 0.0 then IronOxideLAW = 0.0;

{Moisture Adjustment}

BoraxLAW = 0.0;

BoricAcidLAW = 1.76798 * (1 + C-Moisture) * A-b2o3;

KyaniteLAW = 1.69635 * (1 + C-Moisture) * A-al2o3;

LithiumCarbonateLAW = 2.47803 * (1 + C-Moisture) * A-li2o;

OlivineLAW = 2.05128 * (1 + C-Moisture) * A-mgo;

RutileLAW = (1 + C-Moisture) * A-tio2;

SodaAshLAW = 1.70794 * (1 + C-Moisture) * A-na2o;

SugarLAW = (1 + C-Moisture) * A-c12h22o11;

WollastoniteLAW = 2.06905 * (1 + C-Moisture) * A-caO;

ZincOxideLAW = (1 + C-Moisture) * A-zno;

ZirconLAW = 1.51573 * (1 + C-Moisture) * A-zro2;

change this-frit-frac[0] = BoraxLAW;

change this-frit-frac[1] = BoricAcidLAW;

change this-frit-frac[2] = IronOxideLAW;

change this-frit-frac[3] = KyaniteLAW;

change this-frit-frac[4] = LithiumCarbonateLAW;

change this-frit-frac[5] = OlivineLAW;

change this-frit-frac[6] = RutileLAW;

change this-frit-frac[7] = SilicaLAW;

change this-frit-frac[8] = SodaAshLAW;

change this-frit-frac[9] = SugarLAW;

change this-frit-frac[10] = WollastoniteLAW;

change this-frit-frac[11] = ZincOxideLAW;

change this-frit-frac[12] = ZirconLAW;

return this-frit-frac, "[glass-property]";

end

Yueying Deng

Implementation Plan Modeler (Print)

Signature

Date

Rod Gimpel

Requester (Print)

Signature

Date