Melter Downtime Impacts on DFLAW Glass Production and Process Efficiency – 17117

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ABSTRACT

The Hanford Tank Waste Treatment and Immobilization Plant (WTP) pilot studies found that semi-volatile elements started to leave the molten glass pool and enter the offgas stream when the melter became idle. The rate at which the semi-volatile elements leave the molten glass pool follows a typical half-life decay curve. The WTP Direct Feed Low-Activity Waste (DFLAW) program is using existing LAW offgas treatment systems to capture semi-volatile elements leaving the melters. A new building, Effluent Management Facility (EMF), will be built to process effluents generated by the offgas treatment equipment. The effluents are concentrated by evaporation and are recycled to the melter feed streams. Computer modeling studies show that increased amounts of semi-volatile elements in the recycles due to melter downtime adversely impact the DFLAW operations. The extent to which glass productions and process efficiencies are hampered depends upon the frequency, duration, and pattern of the downtime events. Various scenarios were investigated using randomly generated and operator-anticipated downtime schedules. This paper discusses 1) derivation of the volatility half-life curves, 2) downtime schedules, 3) increased amount of semi-volatile elements in recycled material as a result of melter shut down, 4) impacts to glass production and process efficiency, and 5) comparison of scenario results. This study concludes that plant operators can mitigate much of the negative effects of semi-volatile element recycles by managing melter downtime and idle time when possible.

INTRODUCTION

It was noticed in pilot studies that when melters idle semi-volatile elements start to leave the molten glass pool and enter the offgas [1]. The rate at which the semi-volatile elements leave follows a half-life decay function shown in Equation 1. The Vitreous State Laboratory (VSL) in Washington, D.C. noticed that technetium leaves the melter pool with a volatility half-life of three hours.

$$M = M^o \mathrm{e}^{-\lambda t} \qquad \text{(Eq. 1)}$$

where:
M = Remaining mass after t hours (kg)
M^o = Initial mass at time zero (kg)
λ = Decay rate (hr^{-1})
t = Elapsed time since melter shutdown starts (hr)

In addition to technetium, the Hanford tank wastes contain other semi-volatile elements, such as fluorine, chlorine, iodine, chromium, cesium, and sulfur.

Volatility Half-lives of these semi-volatile elements, except sulfur, are directly related to their standard melter decontamination factors[1] (DF). The authors derived the half-life values in Reference [3] based on the melter DF values from Reference [2]. The results are given in Table I.

TABLE I. Hanford Tank Waste Semi-volatile Melter Performance Properties

Element	**Melter DF**	**Melter Retention Fraction**	**Decay Rate λ , hr^{-1}**	**Half-Life $t_{½}$, hr**
Cesium, Cs-137	7.00	0.8571	0.0436	15.90
Technetium, Tc	1.60	0.3750	0.2310	3.00
Chromium, Cr	16.00	0.9375	0.0186	37.3
Fluorine, F	1.88	0.4680	0.1880	3.69
Chlorine, Cl	1.99	0.4974	0.1755	3.95
Iodine, I	2.40	0.5833	0.1406	4.93

A more complicated numerical solution is applied to sulfur volatility half-life because the sulfur DF is a nonlinear function of sulfur oxide and sodium oxide concentrations. The modeling of sulfur is not discussed in this paper but rather documented in Reference [4].

DESCRIPTION

Figure 1 shows a simplified schematic of the DFLAW treatment system as presently envisioned and modeled. In Figure 1, treated feed from a proposed Low-Activity Waste Pretreatment System (LAWPS) is transferred to the concentrate receipt vessel (CRV) where the EMF evaporator concentrate is also added for feed and recycle blending. The blended feed is pumped to the downstream melter feed preparation vessel (MFPV) where glass forming chemicals are added based on the blended feed compositions. Subsequently, the blended feed with glass forming chemicals are pumped from the melter feed vessel (MFV) into the LAW glass melter.

The feed enters the melter from the top and forms a cold cap layer on top of the melt pool. Volatile components in the feed are evaporated or decomposed, then drawn off through the melter offgas system. Nonvolatile components react to form oxides or other compounds dissolved in the glass matrix. It is the semi-volatile elements that behave somewhere between the two such that they end up in the offgas and the glass. With the melter running, the glass portions of the semi-volatile elements would have been poured into LAW glass containers and left the DFLAW processes. However, when the melter feed is stopped due to scheduled maintenance services and unscheduled equipment breakdowns, the cold cap decomposes, and the semi-volatile elements escape from the glass matrix and re-enter the DFLAW systems.

The semi-volatile elements from the melters are captured in the LAW offgas system. The captured semi-volatile elements are then transported to the future EMF where the semi-volatile elements are concentrated and returned to the CRV.

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[1] *The effectiveness of a piece of process equipment removing an analyte of interest is denoted by its DF, which is the analyte's mass entering the process equipment divided by mass leaving the process equipment. Thus, if 10 kg enters and 2 kg leaves, the equipment has a DF of 5 (i.e., 10kg/2kg = 5).*

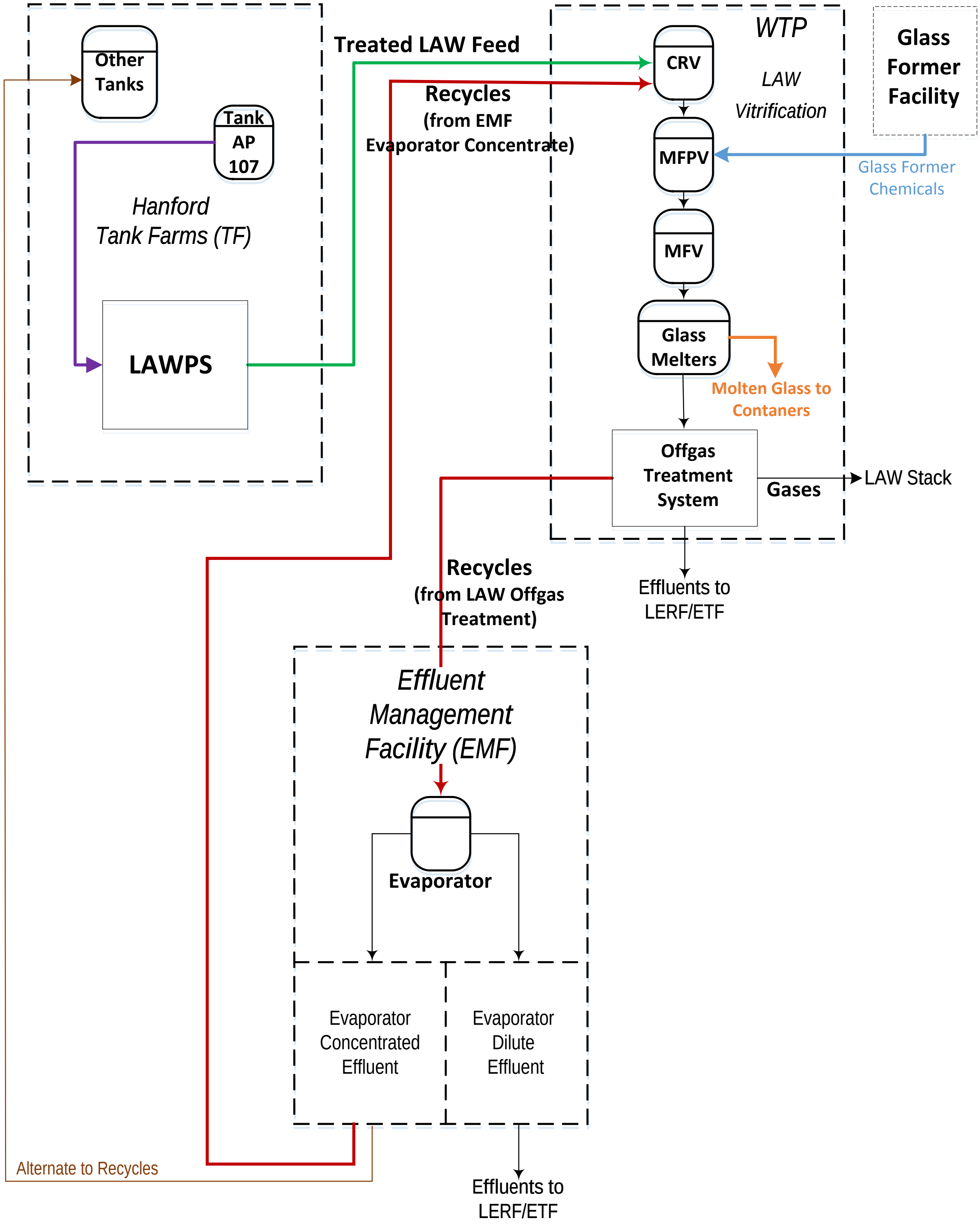

Fig. 1. Simplified Schematic of the DFLAW Treatment System.

Besides increasing the severity for corrosion, higher concentrations of halides and sulfur in the melter feed can lower waste loadings[2] of the glass produced, which will increase glass quantities and extend processing time. This paper focuses on understanding the adverse impacts of halide and sulfur chemistry changes to DFLAW glass production and process efficiency due to melter downtime events.

An operations research (OR) model was used to develop a probable downtime schedule, where downtime events and downtime durations are generated randomly based on the equipment mean time to fail (MTTF) and mean time to repair (MTTR) data, respectively. This downtime schedule was then incorporated into WTP's G2 model[3] for analysis. Table II shows an excerpt of the downtime schedule output by the OR model.

TABLE II. Excerpt of Downtime Schedule from OR

Event	Melter 1 Down Time	Melter 1 Up Time	Melter 1 Duration, hr	Melter 2 Down Time	Melter 2 Up Time	Melter 2 Duration, hr
1	631	651	19.52	631	651	19.5
2	1,768	1,799	30.57	757	789	31.6
3	1,916	1,927	11.61	1,498	1,525	26.9
4	2,184	2,360	175.56	1,691	1,702	10.7
5	2,909	2,946	37.49	1,768	1,799	30.6
6	3,935	3,953	17.12	1,916	1,927	11.6
7	4,136	4,143	6.64	1,975	1,980	4.9
8	4,443	4,518	75.00	2,214	2,222	7.7
9	4,717	4,754	37.55	2,503	2,527	23.2
10	4,852	4,881	29.92	2,909	2,946	37.5

Treatment Duration: 210,700 hr
Melter 1 Total Events: 785 Average Downtime: 47.60 hr (17.73%)
Melter 2 Total Events: 789 Average Downtime: 54.06 hr (20.24%)

The OR model provides an operational schedule that approximates unexpected events when the melters go down and then come back online. Consequently, the OR schedule is not cyclic, but rather, appears more random since it attempts to approximate reality. On the other hand, Savanah River National Laboratory and Washington River Protection Solutions want to evaluate melter downtimes based on operator-anticipated facility availability, for example, 80%, 70%, and 60% time available, which are equivalent to 20%, 30%, and 40% downtimes. The scenarios investigated and presented this report include:

- *Baseline* *No melter downtimes* *(0% downtime)*
- *OR Schedule* *Random events based on MTTB/MTTR* *(~20% downtime)*

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[2] *Waste loading is the percentage of the glass mass comprised of Hanford tank waste. Mass is calculated as oxide(s). For example, sodium as Na_2O, calcium as CaO, and sulfur as SO_3.*

[3] *The Dynamic Model, known at the Hanford site as "G2" is developed using the object-oriented programming platform of Gensym® G2 Bundle Version 8.1.*

- *Cycle A* *8 days operating followed by 2-day outage* *(20% downtime)*
- *Cycle B* *5 days operating followed by2-day outage* *(~30% downtime)*
- *Cycle C* *3 days operating followed by 2-day outage* *(40% downtime)*
- *Cycle D* *10 days operating followed by 4-day outage* *(~30% downtime)*

RESULTS

A comparison of the key performance parameters for each of the scenario runs is given in Table III. The table shows the metric tons of semi-volatile elements fed to the melters, which include the amount from the Hanford tanks (in parentheses) and the amount from recycles. The table also shows the metric tons of glass produced and the numbers of immobilized low-activity waste (ILAW) glass containers. The time to process the waste is also shown for each scenario.

TABLE III. Comparison of Key Performance Parameters

Scenario:		**Baseline**	**OR**	**Cycle A**	**Cycle B**	**Cycle C**	**Cycle D**
Up:Down, days		**1:0**	**Random[1]**	**8:2**	**5:2**	**3:2**	**10:4**
Parameter	**Units**						
Sodium (9,717 before recycle)	MT	10,380	10,764	11,114	11,983	14,369	10,944
Chlorine (174 before recycle)	MT	314	343	363	393	457	289
Fluorine (33 before recycle)	MT	64	70	74	81	93	63
Sulfate (377 before recycle)	MT	409	435	460	511	639	388
Tc-99 (0.40 before recycle)	MT	1.04	1.16	1.23	1.38	1.66	1.02
Water (66,672 before recycle)	MT	91,092	96,556	97,428	104,538	124,788	81,222
Glass made	MT	81,427	87,697	93,991	108,404	150,071	91,764
Waste Sodium Oxide in glass	wt%	16.06%	14.92%	13.92%	12.07%	8.72%	14.22%
ILAW Glass Containers	each	14,782	15,921	17,063	19,680	27,244	16,704
Duration	years	7.65	9.70	10.94	14.03	22.93	11.96

[1] This is per the random OR schedule described earlier and excerpt shown in Table II.

Comparisons indicate that there are negative impacts on DFLAW operations for each downtime scenario when compared with the baseline. Performance measures, such as glass containers and mission duration, deteriorate when downtime frequencies arise. The severity of impacts increases exponentially for Cycles A, B, and C when downtime frequencies change from 20% to ~30% to 40%. This is easily understood that more downtimes cause more semi-volatile elements to escape the melters and recycle to melter feeds, resulting in longer processing time and more glass made with lower waste loadings. With the same downtime of about 30%, Cycle B with a 5:2 schedule performs worse than Cycle D with a 10:4 schedule. This phenomenon can be explained with Equation 1 where decay rate decreases exponentially as a function of time. Also having about the same 20% percent downtime, Cycle A with a repeating 8:2 pattern performs worse than the OR schedule with a random pattern. Analysis shows that the repeating pattern due to timing can magnify the impacts of recycles.

The cycling sequence continues to increase semi-volatile elements and decrease glass production until an equilibrium is reached. When this happens depends upon the scenario's prescribed downtime cycle and the feed that is being processed. Response to the varying feed from the Hanford Tank Farms can be seen in the charts provided in the following figures. Figure 2 is a collection of charts that show the process time that is required between batches that are fed to melters (for each of the scenarios). The charts show markedly increased batch times for the cyclic scenarios. Only the first year is shown in the figures to show better resolution of the times between batches. The cyclic scenarios show behavior that magnify cycle amplitudes.

Figure 3 shows sodium and waste loadings of the glass during the treatment campaign. Notice that the cyclic scenarios also obtain periods of high sodium and waste loadings of the glass. This is because there are less semi-volatile elements in the waste during these periods. However, the lows in the cyclic scenarios are lower and cyclic nature decreases the lows even further. Huge concentration oscillations can happen in some of the scenarios. This is because the recycles can buildup in some of the larger process vessels before being returned to the CRV. The CRV has to then, preferentially, process the "recycles" streams over "waste" streams to prevent the process from becoming saturated with water (water logged).

Chlorine (as chloride) is the main semi-volatile culprit that reduces waste loading in the LAW glass due to recycles. Figure 4 shows chlorine (as chloride) in the target glass during the treatment campaign. Only the last two scenarios are shown due to limited figure space in this paper. The target glass is not the final glass that is disposed with the containers, but rather is the glass that is produced if all the oxides that were in the melter feed batch were made into glass. The target glass contains more chloride, because some is lost to the offgas during the melting process or due to melter downtime. The OR downtimes scenario shows an increase in chloride in the target glass, which is due to recycles. The cyclic scenarios show even more of an increase. The chloride increase stops at 0.70 wt%, which is the maximum allowable concentration in the glass.

Table IV provides a list of key analytes and their average amounts of recycles between the EMF and the WTP. This is the stream that results in the increase of glass production. The recycles are shown as a percentage of the incoming feed from the Tank Farms. Recycle values are given for ^{137}Cs, ^{239}Pu, ^{90}Sr, ^{99}Tc, Cl^-, F^-, Na^+, PO_4^{-3}, and SO_4^{-2}. Fluoride (F^-) recycles even more than chloride (Cl^-) but its concentration is less than chloride and its impact per gram is only 0.6 times that of chloride's impact. Sulfur had little impact on the baseline scenario, but it does have a significant impact on Scenario C where its recycles increases to 69.49% from 9% in the baseline.

TABLE IV. Key Analyte Concentration Averages in the Recycle Stream by Scenarios Extremes

Analyte	Minimum	In Scenario	Maximum	In Scenario	In OR Scenario
Cs-137	32%	Baseline	96%	C – 3:2	32%
Pu-239	0.72%	Baseline	0.82%	C – 3:2	0.79%
Sr-90	0.83%	Baseline	0.88%	C – 3:2	0.87%
Tc-99	163%	Baseline	319%	C – 3:2	194%
Cl^-	31%	Baseline	163%	C – 3:2	98%
F^-	93.77%	Baseline	182%	C – 3:2	112%
Na+	1.19%	Baseline	1.23%	C – 3:2	1.22%
PO_4^{-3}	1.05%	Baseline	1.14%	C – 3:2	1.09%
SO_4^{-2}	9%	Baseline	69.49%	C – 3:2	15.33%

CONCLUSION

Semi-volatile elements that have escaped from molten glasses during melter downtimes re-enter the DFLAW process systems. These semi-volatile elements would have been poured to ILAW glass containers if melter idling did not take place. Recycled semi-volatile elements, especially chlorine, fluorine, and sulfur negatively affect the DFLAW operations, including the glass productions and process efficiencies. DFLAW performance improves when downtime percent decreases. A lower downtime frequency in operations produces better results than the higher frequency counterpart given that the two have the same percentage of downtimes. A downtime schedule with randomly occurring events outperforms a downtime schedule with repeating patterns; therefore, it is concluded that the DFLAW plant operators can mitigate much of the negative effects of semi-volatile elements by managing melter downtime and idle time when possible. The G2 data and more figures, tables, and interpretation of the G2 scenario runs are documented in References [4, 6]

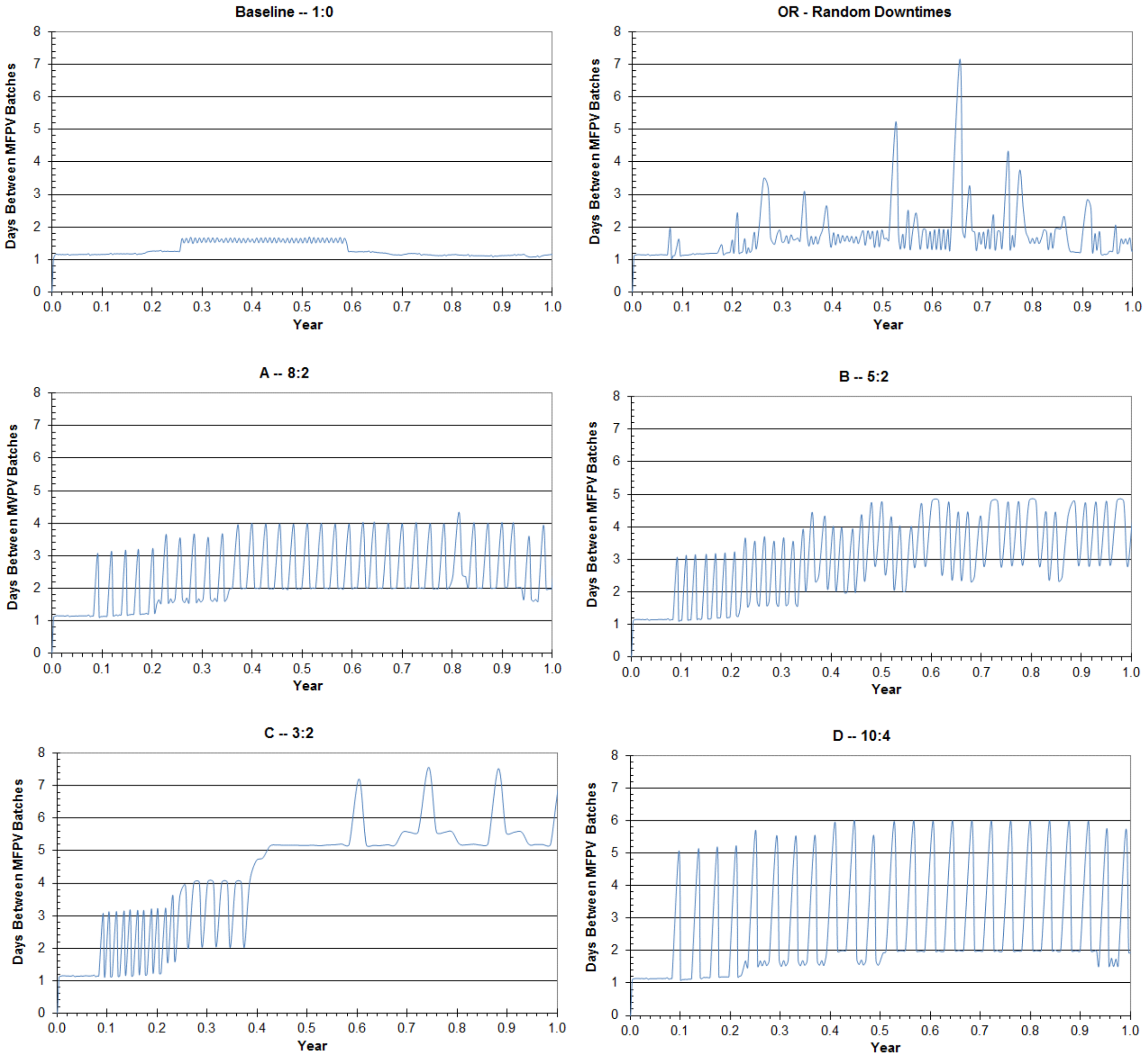

Fig. 2. Days Between Melter Feed Batches for Each Scenario – 1st Year.

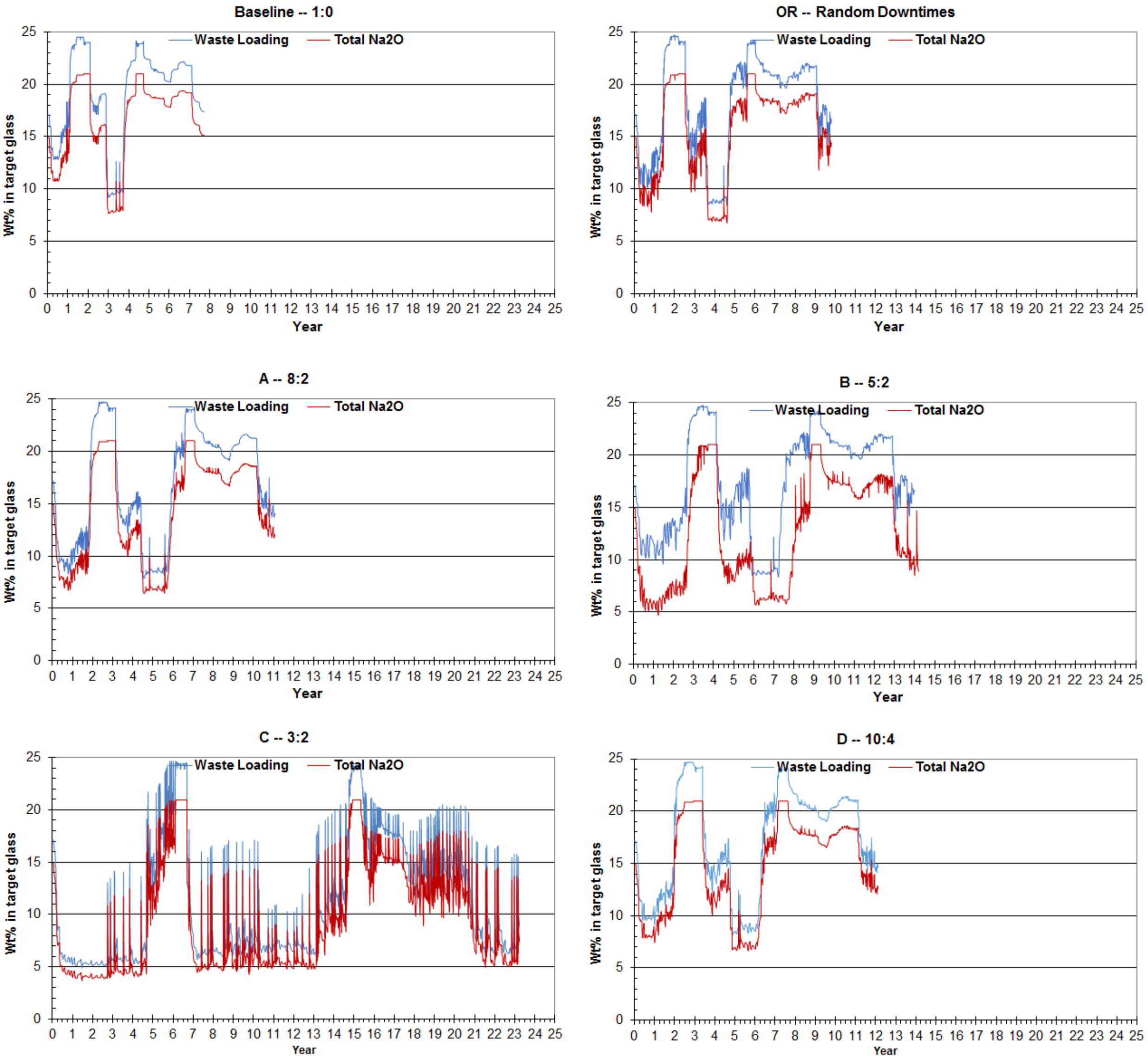

Fig. 3. Waste Loading and Total Sodium in LAW Glass for Project Duration.

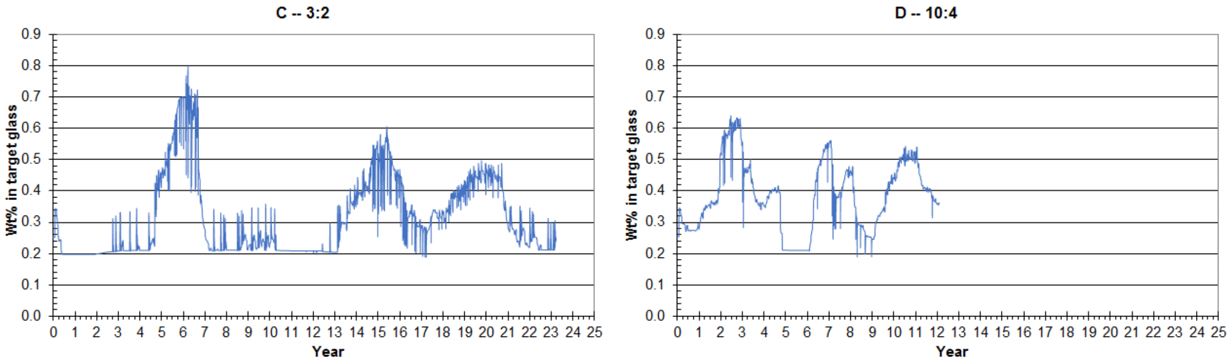

Fig. 4. Chlorine in the Glass.

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