Technology of Off-Gas Treatment for Liquid-Fed Ceramic Melters

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May 1985

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TECHNOLOGY OF OFF-GAS TREATMENT FOR
LIQUID-FED CERAMIC MELTERS

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ABSTRACT

The technology for treating off gas from liquid-fed ceramic melter (LFCMs) has been under development at the Pacific Northwest Laboratory^(a) since 1977. This report presents the off-gas technology as developed at PNL and by others to establish a benchmark of development and to identify technical issues. Tests conducted on simulated (nonradioactive) wastes have provided data that allow estimation of melter off-gas composition for a given waste. Mechanisms controlling volatilization of radionuclides and noxious gases are postulated, and correlations between melter operation and emissions are presented. This report is directed to those familiar with LFCM operation.

Off-gas treatment systems always require primary quench scrubbers, aerosol scrubbers, and final particulate filters. Depending on the composition of the off gas, equipment for removal of ruthenium, iodine, tritium, and noxious gases may also be needed. The ejector-venturi and submerged bed scrubbers are both acceptable as primary scrubbers but have important design and operating differences: the Hydro-Sonic® scrubber and high efficiency mist eliminator are effective for removing aerosols, but again have differences important to design and operation. Ruthenium, iodine, and tritium (as HTO) can all be removed by appropriate sorbent beds, but other means are available which may be advantageous in some cases. Nitrogen oxides are the most common noxious gases requiring treatment, and can be controlled by aqueous absorption or catalytic conversion with ammonia. High efficiency particulate air (HEPA) filters should be used for final filtration.

The design criteria needed for an off-gas system can be derived from emission regulations and composition of the melter feed. Conservative values for melter off-gas composition can be specified by statistical treatment of reported off-gas data. Statistical evaluation can also be used to predict the frequency and magnitude of normal surge events that occur in the melter.

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SUMMARY AND CONCLUSIONS

Vitrification of high-level liquid nuclear waste in the liquid-fed ceramic melter (LFCM) is the reference process for immobilization of both commercial and defense wastes. The high operating temperature of the LFCM volatilizes many of the feed components, and treatment for radionuclide capture and noxious gas abatement is necessary. This report summarizes the status of off-gas treatment technology, and is directed toward those familiar with LFCM operation. Three areas of technology are addressed: characterization of melter emissions, performance of equipment tested for emission control, and system design considerations.

Melter off-gas flow is characterized by surges that occur when liquid feed material flows from the cold cap (feed pile) onto the surface of the molten glass pool. The surge magnitude and frequency are determined by the cold cap behavior, which is a function of the feed composition. When melter feeding is terminated, the cold cap melts into the glass and the plenum temperature rises. The higher temperature causes an increase in the concentrations of some off-gas components, but the rate at which they are evolved does not increase.

Melter exhaust composition is strongly influenced by melter feed composition. Halogens and boron form compounds that are strongly evolved from the melter. Ruthenium is strongly evolved when the feed is oxidizing, but is almost completely suppressed when the feed is reducing. Ruthenium may also form a slag in the bottom of the melter.

The oxidation states of various melter off gases indicate the melter processing conditions. The NO_2/NO ratio can be used as a measure of the redox state in the melter, and the CO_2/CO ratio indicates the oxidizing power of the feed. The total off-gas flowrate gives an indication of the overall processing stability in the melter.

Several factors must be considered in choosing the most conservative conditions for off-gas system design. The important losses from the melter are manifested as particulate material transported through the off-gas system. The particulate material is a combination of entrained feed and volatilized feed components that have recondensed to form solid aerosols. Of these, almost all

radiologically important losses are semivolatile aerosols. The use of forced convection air bubblers in the melter slightly increases losses due to entrainment, but has no other significant effect. The emission rate of semivolatiles during melter idling is lower than the emission rate during normal feeding conditions, even though the plenum temperature is much higher.

Up to six different unit operations may be required for control of off-gas emissions. These include primary scrubbing, aerosol capture, noxious gas removal, ruthenium sorption, iodine sorption, and final filtration.

The submerged bed scrubber (SBS) and the ejector-venturi scrubber (EVS) are effective as primary scrubbers, and are similar in scrubbing and gas cooling performance. However, the EVS requires a pump to supply scrubbing energy while the SBS is passive and requires a substantial pressure drop in the gas.

A high efficiency mist eliminator (HEME) and a Hydro-Sonic® scrubber (HSS) have been tested for removal of solid aerosols, and have exhibited comparable collection performance. However, there are important operational differences. The HEME creates a pressure drop to the off-gas system while the HSS induces a slight draft, and the HSS requires a pump and tank for recirculation while the HEME is passive and requires no ancillary equipment.

Two methods for controlling nitrogen oxide emissions may be applicable to LFCM off-gas systems. These are aqueous absorption, and catalytic conversion with ammonia to benign compounds. The mechanism of aqueous absorption is not well understood, and design for LFCM service will require data for low concentration absorption. Because the requirements for removal are generally easy to attain, absorption will be a strong candidate for treatment. Catalytic conversion has the disadvantage of being more complex and more difficult to operate. These processes should be applicable to vitrification off-gas systems without a major development effort.

There is little evidence that gaseous ruthenium exists in the off-gas following the quenching and cooling stages. However, this element is known to have volatile species that are difficult to remove, so it may be prudent to include provision for control. Methods include sorption on silica gel and molecular sieves, and catalytic reduction at high temperatures on substrates

doped with various transition metals. Sorption has been found to reverse in certain conditions, and catalytic reduction may offer a more reliable solution. However, more testing will be needed to evaluate candidate transition metals for this service.

All iodine fed to the melter will probably volatilize, and can be captured in the off-gas system with various solid sorbents, including charcoal, macroreticular resins, and silver-exchanged zeolite or mordenite. Of these, the most promising is silver mordenite. Because the technology for iodine capture has been developed for reprocessing of high-level waste in which concentrations are much higher, application to the LFCM off-gas system represents a less demanding requirement for the same technology.

Filtration of the existing off gas is necessary to ensure collection of all solid material. High efficiency particulate air (HEPA) filters are needed for this last stage, and very high efficiencies are expected. Filter element life is directly related to the concentration of particulate material in the gas stream, and cannot be accurately estimated without testing. Because these filters are disposable, their deployment in the off-gas treatment system will depend on having reasonable lifetimes, and further testing is needed.

Criteria for off-gas system design can be derived by determining the emission limitations imposed by regulations (e.g., 10 CFR 20), and relating them to the melter emissions predicted for the particular melter feed composition and feed rate. Existing data will permit estimation of the melter off-gas composition for a given melter feed composition; the off-gas flowrate can also be predicted using existing correlations. From this information the off-gas treatment required can be established, and appropriate equipment can be selected. Conservative design values for melter emissions can be established by using statistical methods to evaluate reported data.

The maximum surge event for off-gas must be defined for melter design, and can be predicted from analysis of melter tests of long duration. The frequency and magnitude of these surges can be correlated statistically, and extrapolated to some maximum credible value. Using extrapolated values, the design value

can be determined. Because there are few melter test data from long-duration operations, no general correlation can be established. Additional long-duration tests are needed.

Instrumentation for off-gas systems must maintain the melter vacuum within design limits, adjust the dilution of the off-gas to prevent flammable mixtures, and adjust flowrates to maintain gas velocity and temperature within a prescribed range. A process computer is necessary to accept input from these several points and respond according to established priorities.

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STATUS OF LFCM OFF-GAS TREATMENT TECHNOLOGY

1.0 INTRODUCTION

The liquid-fed ceramic melter (LFCM) converts liquid radioactive waste to the stable form of glass castings (Buelte and Chapman 1979). There are three principal support systems for the melter: the feed pretreatment and transfer system, glass containerization system, and off-gas treatment system.

The melter and its supporting systems have been undergoing continual development since the conception of the process in 1974 (McElroy 1975). Ultimately, the LFCM process will vitrify liquid waste stored at Hanford (Washington), Savannah River (South Carolina), and West Valley (New York). Additionally, the process has been chosen for solidification of high level wastes resulting from reprocessing of civilian spent nuclear fuel in Europe and any such future wastes in the U.S. Though the facility to be operated at Savannah River is already under construction, melter systems for civilian reprocessing waste, and for Hanford and West Valley waste are in early design phases. These developing systems will be the principal beneficiaries of the design-related information in this document.

This report documents results of work done at Pacific Northwest Laboratory (PNL) on the characterization of melter emissions and testing of off-gas equipment. These results are from nonradioactive, pilot-scale melters processing simulated high-level waste. Related work performed at other laboratories will be reviewed and discussed. Most other work in the U.S. has been performed at Savannah River Laboratory, while foreign work has been done primarily by the Karlsruhe Nuclear Research Center of the Federal Republic of Germany, the Power Reactor and Nuclear Fuel Development Corporation of Japan, and the Nuclear Energy Research Center in Belgium. Detailed design information is not presented; rather, general system-design considerations such as turndown requirements, materials of construction, remote operation constraints, and equipment lifetimes will be discussed. This report is intended for those familiar with operation of the LFCM.

2.0 DESCRIPTION OF LIQUID-FED CERAMIC MELTER

During operation of an LFCM, an exhaust stream is generated that is comprised of air, steam, gases from reaction or decomposition of feed chemicals, solid aerosols from feed materials, and volatile or semivolatile metal compounds. The off-gas system treats this stream to permit discharge of the final noncondensable gases to the atmosphere. Following is a brief description of current pilot-scale LFCM's and those envisioned for full-scale operation.

The slurry-fed, joule-heated glass melter operates on the same basic principle as the large number of commercial electric melters in the glass industry. Molten glass is contained within a cavity made of corrosion-resistant refractory. In melters designed to date by PNL, the glass contact refractory is surrounded by additional layers of lower density backup and insulating refractories, which provide secondary glass containment and added thermal insulation. The glass is uniformly joule-heated by passing an alternating current between electrodes in contact with the molten glass.

The concentrated waste slurry, which is fed directly into the melting chamber, is normally separated from the molten glass by a crust of dried and calcined solids known as the cold cap. The cold cap is a stable material which is relatively nondispersible. The cold cap typically covers the majority of molten glass surface (70 to 90%), which helps to suppress volatilization. Heat is transferred from the molten glass through the floating crust to the aqueous pool of slurry. Gases and steam produced during calcination of the crust, percolate up through the crust and aqueous pool. Periodically, the aqueous pool comes in direct contact with the molten glass through cracks or vent holes in the crust.

The melter is encased in a supporting metal box or shell to contain effluents that could penetrate the refractory material. The three melter designs for high-level waste processing in the U.S. are those to be used at West Valley, Hanford and Savannah River. The off-gas systems for these melters were designed based on extensive pilot-scale nonradioactive tests and operation of a laboratory-scale radioactive melter. The Hanford design is conceptual; prototypes of those at West Valley and Savannah River are scheduled for

nonradioactive testing in the near future. A schematic of the pilot scale ceramic melter (PSCM) at PNL is given in Figure 2.1 and it is from this melter that most of the experimental results to be discussed in this report were obtained. The PSCM is about 1/4 to 1/3 scale as compared to the three major U.S. designs.

FIGURE 2.1. Schematic of Pacific Northwest Laboratory's Pilot-Scale Ceramic Melter

3.0 CHARACTERISTICS OF OFF-GAS EMISSION FROM LFCMS

Effluent characteristics of LFCMs are normally discussed in terms of the three main categories shown below:

<u>Gases</u>	<u>Semivolatiles</u>	<u>Particulates</u>
H ₂	Cs	Fe
O ₂	Hg (Cd) ^(a)	Al
CO	Ru	Rare earths
CO ₂	Sb	Sr
NO	Se	Many others
NO ₂	Tc (Mn) ^(a)	
SO ₂	Te	
	B	
H ₂ O	Halogenated compounds	
Halogens		

(a) Used in nonradioactive simulations.

In terms of melter airborne exhaust losses, these three categories can be further simplified into two emission classes: gases and aerosols. The following discussion will describe the characteristics of these LFCM emissions as a function of the following melter operational parameters:

- feed composition
- feed rate
- feed nozzle positioning
- cold cap development
- plenum height
- plenum temperature
- forced glass convection
- glass temperature
- inleakage.

3.1 GASEOUS EMISSION

The composition and temporal nature of melter-generated gas emissions are strong functions of feed composition. Both the elemental and chemical natures of the feed components are important in establishing relative proportions of the various gaseous byproducts produced during LFCM feed processing. This fact is illustrated by the behavior of carbonaceous reductants in the feed. When formic acid is used in LFCM feeds, flammability hazards associated with H_2 and CO in the quenched melter exhaust are major process concerns. Substitution of an equivalent quantity of a more refractory reductant, such as sugar, corn-starch, or coal, presents no such combustion hazard. Of course, other operational parameters, such as plenum temperature and melter inleakage, can also be used to influence melter exhaust gas composition. The Defense Waste Processing Facility (DWPF) being constructed at Savannah River Laboratory (SRL) utilizes both of these parameters to oxidize combustibles before they are conveyed into the off-gas system.

The effect of plenum lid heaters upon the melter exhaust composition is illustrated in Figure 3.1, which characterizes results from a PNL melter test. This test employed 100 h of radiant lid heat boosting, followed by 20 h of unboosted operation. The high plenum temperatures associated with lid heating have a definite controlling influence on the combustible gases CO and H_2 . The data presented in this figure also illustrates that melter emissions are not generated smoothly or continuously even under the most controlled operational conditions. This behavior is due to the erratic, nonuniform way in which melter feed is dried, oxidized, and melted during the liquid feeding process. Large variations in gas generation rates usually occur when dammed-up liquid feed lying atop an insulating layer of dry feed (the cold cap) abruptly flows out upon a hot glass surface. The liquid quickly flashes off this hot surface, producing a flow pulse composed of steam and volatile decomposition/reaction products. The frequency and/or extent of these excursions are related to the physical properties of the feed which, in turn, is composition-dependent. Figures 3.2 and 3.3 illustrate the behavior of some of the more important melter-generated gases accompanying flow surges. The frequency and magnitude of these surges are positive indicators of melter system instabilities, which are most

FIGURE 3.1. Melter Exhaust Gas Composition of a 100-h Boosted, 20-h Unboosted Test

FIGURE 3.2. Compositional Behavior of Noncondensable Melter Exhaust Gases Accompanying a Flow Surge. (Maximum extent of the surge event: flow: 3X; $H_2 < 3.5\%$; $Co \gg 0.5\%$; CO_2 -15%; C_2 -17%)

FIGURE 3.3. Noncondensable Off-Gas Composition Preceding and During Melter Reboil

often associated with erratic or excessive feeding. One of the instabilities is reboil, which is caused by glass redox changes, and involves rapid evolution of oxygen.

The correlation between the emission rates of noncondensable gases and steam flow surges suggests a prompt evolution of combustible gases from the cold cap. Figures 3.4 and 3.5 portray the time-dependent compositional behavior of the melter exhaust streams upon feed interruption or termination. With the exception of SO_2 , none of the melter-generated gases increased in concentrations when feeding was terminated. Consequently, a dry cold cap has not been observed to produce combustibility hazards that are greater than those already existing during normal liquid feeding.

Feed components that have the greatest influence on melter exhaust gas composition are traditionally chemical additives used in waste processing (NO_3^- , SO_4^{2-}) or in feed conditioning (organics). Because these elements all possess several volatile oxides, the exhaust conditions will vary depending on the nature of the feed, as well as plenum temperature. Table 3.1 generalizes exhaust conditions based upon PNL observations involving these parameters.

Other chemical additives such as the halogens (particularly I_2) are also evolved as gases in both elemental and chemically combined states. Mercury, a chemical component in SRP defense waste which itself is a semivolatile, has been found at PNL to evolve from LFCMs predominantly as a halogenated compound (Hg_2X_2). The glass-forming additive boron also forms volatile compounds which are strongly evolved during LFCM feed processing. In high-level liquid waste, because tritium is predominantly in the form of water (HTO), it is completely volatilized in the melter.

The volatility of the feed components mentioned up to this point are not dramatically affected by the overall composition of the feed. This is not the case for the waste component Ru. Ru is strongly evolved as a gas when the feed waste stream is oxidizing. However, the oxidizing strength of the feed is lowered by denitration or addition of a reductant to control the oxidation state of the glass produced, gaseous evolution of Ru effectively ceases. In

FIGURE 3.4. Compositional Behavior of Exhaust Stream Upon Feed Interruption

FIGURE 3.5. Melter Off-Gas Compositional Behavior Associated with Feed Termination. (The $t = 30$ min compositional spike is due to the injection of a small quantity of liquid feed.)

TABLE 3.1. Qualitative Relationship Between LFCM Feed Types and Presence of Exhaust Gas Constituents

Feed Type	Plenum Temperature	NO ₂ /NO	CO ₂ /CO	H ₂	SO ₂ ^(a)
Nitrate	Low	∞	--	--	No
Refractory organics	Low	--	10	No	No
Formate	Low	--	<3	Yes	No
Formate	High	--	≥10	No	Yes
Nitrate/refractory organic	Low	0-∞	≥10	No	No

(a) SO₂ emissions have never been measured directly.
 -- = Data below detection limit.

fact, slag formation under reducing melter conditions can produce Ru loss rates that are as large as those associated with gaseous off-gas system losses under oxidizing conditions.

The exhaust gases generated by an operating LFCM can be used to monitor melter processing conditions. For instance, NO_x and/or CO_x concentrations can be used to monitor feed processing rates. The ratio of the oxides of carbon, if present, can be used to assess the oxidizing power of the liquid feed, e.g., NO₂ concentration. The nitrogen oxide ratio NO₂/NO, on the other hand, has been found to be useful in assessing the redox conditions of the melter glass. In addition, oxygen monitoring of the melter exhaust can diagnose and alarm foaming and/or melter reboil conditions. Finally, as mentioned earlier, the temporal behavior of major exhaust gas components can be a good indicator of melter processing stability.

3.2 AEROSOL EMISSION

LFCM off-gas system losses for most semivolatile and nonvolatile feed components (Hg excepted) are associated with aerosol emission. Table 3.2 summarizes typical LFCM off-gas emission data obtained using a formatted melter feed. The values listed in this table are melter DFs, which are ratios of the rate at which feed components enter the melter, to the rate at which they are evolved. Particulate DFs are partial DFs relating to only a single loss mechanism:

TABLE 3.2. Melter DFs for Particulate and Total Feed Component Using Formated Melter Feed

Element	Average DF	
	Particulate	Total
Al	27,000	22,000
B	6,800	100
Cd	9.9	9.9
Cl	21	2.9
Cs	14	14
Fe	1,900	1,800
La	2,100	2,100
Mn	1,800	1,800
Na	300	300
S	11	5.5
Sr	1,800	1,800
Te	3.0	3.0
Zr	22,000	22,000

aerosol emission. The data presented in this abridged table clearly show that melter gas-phase losses to the off-gas system are only significant for Cl, S, and B, which readily form volatile acid gases previously discussed.

This is not to say that melter-induced volatilization has no influence on melter losses of other feed component elements. On the contrary, the low DFs associated with the semivolatile elements Cd, Cs, and Te, as well as Se and Sb, clearly underscore the importance of this volatilization process. What is being said is that apart from the mechanisms responsible for producing airborne effluents, particulate transport through the off-gas system is the predominant loss mechanism associated with liquid-fed melter operation.

Because most radiological melter off-gas system losses are associated with aerosol emission, establishing the characteristics of these aerosols is of particular interest relative to off-gas system design. The size distribution of melter-generated aerosols have been established at PNL using a cyclonic particle-size analysis system. Table 3.3 details the characteristic manner in

TABLE 3.3. Size Distribution of Melter Aerosols

PNL Experiment No.	Feed Type	Average wt%			
		16 μm	6 μm	1 μm	<1 μm
LFCM-7	Formate	76.7	2.8	8.5	11.9
PSCM-4	Formate	--	0.9	3.6	95.6
PSCM-5	Formate	13.5	3.9	20.2	62.2
PSCM-6	Formate	46.1	0.5	12.7	40.7
PSCM-7	Formate	7.5	3.2	9.4	79.9
PSCM-8	Formate	44.0	7.3	19.6	29.1
PSCM-9	Nitrate	8.2	2.1	1630	73.7
PSCM-15	Nitric acid	44.7	9.8	22.4	23.1

-- = Data below detection limit.

which melter particulate matter is found to be distributed across the cyclonic sample fractions for the many different melter experiments examined. All melter tests, with the exception of PSCM-4, exhibited aerosol-size distributions that were bimodal. This suggests that the overall aerosol distribution is comprised of two independent components, each having its own characteristic size distribution. Gross compositional dissimilarities between the discrete cyclonic size fractions shown in Table 3.4 strongly reinforce this argument. Moreover, because the submicron size fraction shown in this table contains only 12% of the total sample mass, but possesses essentially all the semivolatile matter of the sample, the mechanism responsible for the small diameter component of the overall distribution is probably a volatilization/condensation process that occurs within the melter plenum. The compositions of the large cyclonic size fractions are very similar to those of the slurry feed as shown in Table 3.5. Consequently, the large component of the bimodal distribution is most certainly associated with a gross entrainment mechanism.

Because greater than 50% of LFCM particulate off-gas system losses are associated with aerosols having aerodynamic diameters of 1 μm and below, and essentially all the radiologically important semivolatiles are concentrated in

TABLE 3.4. Typical Elemental Distribution Across the Cyclonic Sampling System

Element	Distribution, %			
	16 μm	6 μm	1 μm	<1 μm
Al	96.2	0.9	2.5	0.4
B	87.8	1.8	7.8	2.6
Ba	83.7	5.8	10.5	0
Ca	77.7	2.7	15.2	4.4
Cd	10.7	0.8	7.9	81.2
Ce	92.1	0	7.9	0
Cr	46.4	21.7	23.3	8.6
Cs	7.5	0	5.4	87.1
Cu	82.6	4.9	4.2	8.3
Fe	77.3	2.6	17.0	3.1
La	91.9	1.5	6.1	0.5
Li	83.2	1.5	5.3	10.0
Mg	91.5	1.6	5.8	1.1
Mn	89.4	6.4	3.6	0.6
Mo	77.5	5.6	9.8	7.1
Na	68.8	1.7	5.6	23.9
Nd	93.4	0	6.6	0
Sb	100.0	0	0	0
Se	56.9	1.9	11.4	29.8
Si	92.0	1.8	5.6	0.6
Sr	77.6	2.8	19.6	0
Te	5.5	0.4	3.2	90.9
Ti	91.2	1.8	6.0	1.0
Zr	91.6	1.6	5.6	1.2

TABLE 3.5. Composition of 16-micron Cyclonic Sample Fraction

Elemental Oxides ^(a)	Weight Percent	
	16 μ m	Feed
Al ₂ O ₃	3.4	5.1
B ₂ O ₃	9.0	10.5
CaO	1.6	1.7
Fe ₂ O ₃	14.4	12.7
La ₂ O ₃	0.3	0.4
LiO ₂	3.5	4.1
MgO	1.1	1.4
MnO	3.2	2.9
Na ₂ O	13.0	13.6
SiO ₂	38.0	45.6
TiO ₂	0.7	0.7
ZrO	0.3	0.4

(a) Assumed oxide forms.

these fractions, melter design parameters such as plenum freeboard and exhaust port and feed nozzle positioning would have little or no effect on off-gas processing design criteria.

3.3 MELTER EMISSION PERFORMANCE

Because most melter off-gas system losses have been shown to be associated with aerosol emission, the off-gas performance (DF) of LFCMs is conveniently measured in terms of gross off-gas aerosol losses. A comparison of the average gross melter DFs obtained from the numerous melter tests conducted at PNL reveals that, irrespective of feed type, when a melter is underfed due to either experimental design or system limitations, extremely high glass conversion efficiencies and aerosol DFs result. Conversely, experiments punctuated by melter overfeeding have, in general, exhibited the poorest off-gas emission performance. In between these two extremes lies the majority of melter tests conducted at PNL where feeding rates were carefully ramped to produce stable steady-state operating conditions which matched feeding and glass production

rates at ~90% cold cap coverage. Table 3.6 compares emission data obtained from LFCM tests conducted under all three of these operating conditions: underfeeding, steady state, and overfeeding.

TABLE 3.6. Emission Data From LFCM Tests Under Various Conditions

Element	Melter DF		
	Under-fed	Steady State	Over-fed
Al	3,500	22,000	190
B	44	100	75
Ca	67	1,200	62
Cd	--	9.9	8.0
Cl	--	2.9	--
Cs	330	14	12
Fe	3,300	1,800	69
La	3,100	2,100	--
Li	2,400	1,300	89
Mg	3,600	7,800	120
Mn	4,500	1,800	76
Na	1,500	300	60
Nd	3,300	2,500	--
Ni	4,200	1,100	--
Ru	3.1	--	16
S	--	5.5	--
Sb	--	--	67
Se	--	--	1
Si	12,000	13,000	120
Sr	2,900	1,800	55
Te	--	3.0	5.6
Ti	4,700	5,900	120
Zr	<u>1,700</u>	<u>22,000</u>	<u>--</u>
Total	1,900	800 ± 80	120 ± 50

-- = Data below detection limit.

It is clear from a process engineering standpoint that a steady-state feeding condition is the most desirable of the three operating alternatives. The maximum feeding rates achievable for a given melter under steady-state conditions can and have been increased through use of auxiliary plenum heaters. The effect of feed boosting on melter performance has been studied under controlled steady-state conditions. These tests were designed to establish the relationships, if any, between absolute feeding rates and melter DF.

Table 3.7 presents gross aerosol DF values associated with the boosted PSCM-5 and PSCM-6 tests. Clearly, these data show no correlation between feed rates and DFs. Moreover, the boosted PSCM-6 experiment did not utilize electric radiant lid heaters for the entire melter test, yet no significant differences in normalized melter emission rates were observed throughout the experiment. Consequently, these data suggest that electric radiant plenum heaters can be employed to boost liquid feeding rates of ceramic melters without deteriorating melter DF.

TABLE 3.7. Steady-State Aerosol Emission Characteristics

PSCM-5 Boosted Test				PSCM-6 Boosted and Unboosted Test			
Sample Identification	Feed Rate, L/h	Particulate		Sample Identification	Feed Rate, L/h	Particulate	
		Loading, mg/L ^(a)	DF			Loading, mg/L ^(a)	DF
A	51	0.55	470	A	68	0.29	820
B	72	0.49	460	B	68	--	810
C	79	0.44	510	C	67	0.37	840
D	81	0.61	440	D	74	0.25	910
E	81	--	370	E	90	0.41	700
F	86	0.48	492	F	91	0.28	840
G	93	0.48	440	G	90	--	720
H	93	--	670	H	58 ^(b)	0.32	870
Average			480	I	58 ^(b)	0.54	660
				Average			800

(a) STP.

(b) Unboosted operation.

-- = Data below detection limit.

Air-sparge-induced glass convection has also been used to boost LFCM steady-state feeding rates. The results obtained from the limited tests conducted indicate that, at worst, a slight lowering of melter DF may result due to increases in gross entrainment. These losses are, however, readily removed by the first stage scrubber. The overall DF across the melter and quench scrubber has not been found to be significantly affected by forced-convective feed rate boosting techniques.

It has been shown previously (Table 3.3) that physical characteristics of LFCM-generated aerosols are nominally independent of feed compositions. However, the composition of these emissions may depend upon the nature of the feed. Table 3.8 compares average elemental DF experiments derived from various feed streams processed by PNL LFCM melters.

A comparison of elemental melter DFs achieved with the various waste slurries processed reveals that, with only a single exception, higher effective emission rates (lower DFs) were observed for the radiologically important semi-volatiles when reducing melter waste was employed. The reducing power of the formic acid feed component apparently promotes volatilization in the plenum and thereby produces greater effective off-gas losses of these elements. Exceptions to this have been observed and conclusive data to support the generalization is presently lacking.

Ruthenium, of course, is the major exception to the above generalization. Oxidizing feeds, as discussed previously, promotes Ru volatility and low gaseous DFs. Reducing feed, on the other hand, totally suppresses Ru plenum volatility to the point that off-gas system losses for this trace element are not detectable.

Karlsruhe Nuclear Research Center in FRG has characterized pilot scale LFCM emissions, based on 2500 hr of nonradioactive operation (Weisenberger et al. 1979). They have presented results on the cumulative loss of feed components in the melter exhaust and the individual losses of Cs and Ru. The overall feed oxide DF was 22, substantially lower than observed with PNL pilot tests (cumulative feed component DF of greater than 500). The Cs DF result was similar, with an average value of 29. In qualitative agreement with results at

TABLE 3.8. Average DFs from Various Feed Streams

<u>Element</u>	<u>Hydroxide</u>	<u>Formate (Reducing)</u>	<u>Nitrate (Oxidizing)</u>
Al	3,200	13,000	450
B	150	190	53
Ca	720	1,200	260
Cd	100	7.5	--
Cl	2.8	4.1	--
Cs	30	28	73
Fe	1,200	1,400	350
La	--	4,100	330
Li	680	1,500	230
Mg	2,600	5,400	374
Mn	1,800	2,700	440
Na	350	370	213
Nd	--	2,400	370
Ni	900	3,300	22,000
Ru	30	--	15
S	8	7.8	21
Sb	950	430	--
Se	--	58	1
Si	4,300	5,900	530
Sr	2,100	1,200	330
Te	130	11	290
Ti	790	6,100	520
Zr	<u>--</u>	<u>10,000</u>	<u>4,900</u>
TOTAL	500	720	260

-- = Data below detection limit.

PNL, Ru losses depend on the presence of nitrate, an oxidant. The average melter DF for Ru when the feed contained 3.4 M HNO_3 was only 8, whereas the DF for denitrated feed was about 30.

3.4 EMISSION DURING MELTER IDLING

Because of the high ($\sim 1000^\circ\text{C}$) plenum temperatures associated with idling joule-heated ceramic melters, volatilization losses of radiologically important glass components during these periods could overwhelmingly influence the overall melter source term. The compositions of two different types of deposits formed in the process off-gas line during melter idling appear in Table 3.9. The data in this table verify importance of the volatilization loss mechanism for the semivolatiles. In order to determine the overall importance of this melter loss mechanism, LFCM elemental emission rates were monitored during and after a 10-day melter test. Emission monitoring after the test continued well beyond the time required for the melter to achieve thermal equilibrium. The only radiologically important elements to exhibit idling emission rates comparable to those occurring during the test were the semivolatiles. The emission behavior of Cs appearing in Figure 3.6 represents a worst case condition for all elements exhibiting significant emission rates during melter idling. The dashed line indicates the time at which melter feeding was terminated. The peaking in emission rate lying to the right of this dashed line is due in part to burnoff of plenum deposits formed during the preceding liquid-fed melter test. The important point is that melter emission rates during idling never exceed the nominal rates occurring during normal LFCM feed processing.

Experiments have also been conducted to establish whether idling emissions could be suppressed or reduced by control of plenum temperature and, consequently, glass surface temperature and viscosity. Temperature control was maintained through use of plenum water sprays, which cooled but did not disturb the surface of the melter glass pool.

This study was initiated immediately after a 120-h liquid-fed melter test. With a 42 L/h water spraying rate and the melter under automatic control to maintain the bulk tank temperatures approximately constant, the melter glass

TABLE 3.9. Melter Idling Deposits

Oxides	Gray Deposits wt%	White Deposits wt%	Glass wt%
Al ₂ O ₃	1.2	0.11	3.7
B ₂ O ₃	14.2	1.6	10.0
CaO	0.22	0.46	1.2
CdO	0.02	0.02	0.009
Cr ₂ O ₃	0.57	0.58	0.02
Cs ₂ O	3.7	8.3	0.05
Fe ₂ O ₃	0.10	0.17	14.8
K ₂ O	0.79	0.85	(a)
Li ₂ O	1.92	2.6	4.4
MgO	0.05	0.05	1.4
MnO ₂	0.05	0.05	3.9
Na ₂ O	31.0	31.0	15.7
NiO	0.25	0.02	1.2
RuO ₂	0.82	2.1	0.01
Sb ₂ O ₃	0.01	0.01	0.02
SiO ₂	0.02	0.47	45.1
SrO	0.005	0.005	0.02
TeO ₂	0.70	0.70	0.002
TiO	0.01	0.01	0.8
ZnO	0.02	0.02	0.008

(a) Used in sample preparation.

surface was cooled to the point that it formed a continuous, nonconvective layer above the bulk melter glass pool (with plenum at 280°C). When the spray rate was decreased to 27 L/h, the surface temperatures increased and the viscosity decreased significantly. In addition, convective mixing opened vents in the glass surface that migrated at random across the glass pool. However, plenum temperatures were not high enough to melt feed deposits formed upon the melter walls and lid during the preceding PSCM-5 experiment. Finally, the

FIGURE 3.6. Time Distribution of Cesium Emission

cooling spray was terminated and the melter was allowed to idle, which slowly brought the melter plenum up to 850°C. Samples were collected from the plenum during all phases of this study.

The results obtained from these plenum samples are graphically summarized in Figure 3.7, which characterizes the emission rates of the semivolatile elements under various idling conditions (temperature) employed during this test. These data indicate that emission rates of all semivolatile elements decreased as a function of time after the completion of PSCM-5 at a 42 L/h water-spraying rate. Reducing the cooling spray rate to 27 L/h increased both plenum temperature and semivolatile emission rates; however, an equilibrated plenum temperature was not achieved during the brief 24-h period of reduced spraying.

Termination of the water-cooling spray increased the plenum temperature steadily to the point where plenum surface deposits formed during PSCM-5 began to melt and "burn" away. The dramatic peaking of emission rates of the semivolatile elements occurred during this period. The emission characteristics under these plenum warmup conditions are very similar to those observed during the previous melter idling test.

FIGURE 3.7. Emission Rates of Semivolatile Elements During Melter Idling

4.0 OFF-GAS EQUIPMENT PERFORMANCE

The off-gas processing systems of LFCMs control aerosols, gaseous radioactivity, and noxious gases. This chapter identifies and describes currently envisioned process equipment and technology for control of these emissions, and characterizes their scrubbing performance.

The off-gas system may require up to six stages. In the first stage, gross aerosols are removed and hot exhaust gas is quenched. This may be followed by submicron-aerosol removal devices. Most of the work done on off-gas system studies has focused on melter discharges and the performance of these first two quenching and aerosol removal stages.

At PNL, the pilot scale ceramic melter (PSCM) has been used for most off-gas studies. The PSCM off-gas system has a volume capacity of about 200 ft³/min. PSCM gas-cleaning equipment to be discussed in this section includes an ejector-venturi scrubber, submerged bed scrubber (SBS), high-efficiency mist eliminator (HEME), and Hydro-Sonic® scrubber. The arrangement of these components is shown in a simplified schematic in Figure 4. Additional PSCM equipment, not shown in Figure 4.1, includes a packed column for gas scrubbing, sorbent bed vessels, a HEPA filter, and a thermosyphon evaporator. A piping and valve network (of which some segments are omitted from Figure 4.1 for clarity) allows for numerous equipment sequences, including those that resemble the off-gas systems planned for use at Hanford, West Valley, Savannah River, and for a melter that would treat civilian reprocessing waste. Individual equipment pieces and their performance will be described in more detail in sections that follow.

Up to four more treatment stages may be needed in an LFCM off-gas system but, to date, there has been limited operating experience for these devices with an actual LFCM. Depending on feed composition, a step for scrubbing hazardous or highly corrosive gases maybe needed. Depending on the radioactive inventory of the waste, equipment may be needed to remove gaseous iodine and ruthenium. The final treatment step includes HEPA filtration, either in the process cell, or in the facility ventilation system prior to stack release, or in both places. Much of the material to be presented on these last four devices will be based on experience in other, related applications.

FIGURE 4.1. Arrangement of Air-Cleaning Equipment in PSCM Off-Gas System

4.1. PRIMARY SCRUBBERS

The purpose of the first scrubbing stage is to cool melter exhaust and remove the larger aerosols from this stream. During feeding periods, the plenum gas temperature, as measured on the PSCM, typically ranges between 300 and 400°C without plenum heat. At these temperatures, entrained solids tend to adhere to pipe walls, so air cooling via injection has been proposed for the West Valley and Hanford process off gas (POG) systems (Section 5.0). By the time the melter exhaust and injected air reaches the primary scrubber, the temperature has been lowered significantly. Additionally, with so much added air, the dew point of the off gas is quite low so that little steam condensation may occur. In the SRL design for DWPF, the melter employs lid heaters which boost the off gas to 600-800°C. It is proposed to use an air/steam injection for pipe-wall cooling; the primary scrubber in this application will thus remove most of this added steam.

Aerosols larger than 1 micron account for between 20 to 80% of the solid emissions in melter exhaust. The primary scrubber should be capable of removing most of the material in this size range. There are many scrubbing devices that could perform this duty and also affect cooling but the primary scrubbers that have received the most attention in the U.S. programs are the commercially available ejector-venturi, and a new system, the submerged bed scrubber (SBS).

Both Hanford and DWPF designs call for an ejector-venturi scrubber (also called a jet or eductor scrubber). This scrubber has been used for many types of industrial emissions since the early 1960s. As shown in Figure 4.2, the device utilizes a high-pressure spray nozzle that atomizes liquid to particle-collecting droplets. These units have a large water consumption compared to other scrubbers, being 50 to 100 gal. per 1000 ft³ of gas handled. The liquid spray stream provides motive force for the gas; rather than a pressure drop, a draft of several inches water can be developed. High relative velocity between liquid droplets and gas aids in separating the two streams (Calvert et al. 1972). Harris (1966) describes the three major activities of the ejector-venturi: 1) impaction of the fume particle by a larger size, faster moving water droplet, 2) retention or capture of the particles by the water drop, and

FIGURE 4.2. Principle of Operation of Ejector-Venturi Scrubber, from Ametek Brochure

3) removal or separation of the water drop containing the particle from the air or gas stream. Separation is generally accomplished with a simple gas reversal chamber.

The ejector scrubber has been selected over other scrubber types for LFCM service because it is effective for aerosols down to 1 micron in size, is compact and thus requires little radioactive process cell space, is simple to operate, has few vulnerable internal components, and a given unit can accommodate wide variations in inlet gas volume, temperature, and composition. The major peripheral equipment for the ejector scrubber are a recirculation pump and a tank for storage of liquid.

The SBS is a packed bed submerged in a vessel in which gas to be cleansed enters at the bottom of the bed; buoyancy drives liquid recirculation as the gas is pulled upwards via the POG system blowers. This recirculating fluid transfers heat from the hot melter-emitted gas and provides for gas scrubbing and cleaning of the bed. These processes are shown in the schematic of Figure 4.3. As liquid and gas make concurrent contact in the bed, the liquid is heated. The outer portion of the vessel is fitted with cooling coils to remove

FIGURE 4.3. Principle of Operation of Submerged Bed Scrubber

this heat. Because of this internal recirculation, no external pump is needed, a significant advantage because scrub liquid is abrasive and usually corrosive. However, the pressure drop through the bed is high, being set by the submergence of the inlet gas pipe; for the current design phase for West Valley this is about 48 in. The SBS is based on an original design known as a submerged gravel scrubber, which was developed for capturing aerosols during an emergency vent of a nuclear reactor containment structure (Hilliard et al. 1981).

The primary scrubber used at Karlsruhe, FRG is a plate column (Weisenburger 1979). A schematic of this device is given in Figure 4.4. Melter exhaust enters through the dip leg submerged in the liquid vessel. Scrub solution is recirculated counter-currently to the upward moving process gas. At Karlsruhe, the system is operated at saturated conditions, so there is minimal condensation of melter-emitted steam.

The following two subsections discuss the emission control of aerosols and gaseous radioactive effluents functions for both the ejector-venturi scrubber and the SBS.

4.1.1 Aerosol Collection Performance of Primary Scrubbers

Because, by design, quench scrubbers are low-efficiency devices capable of removing only large diameter airborne particulate matter, one would expect the

FIGURE 4.4. Primary Scrubber (Plate Column) Used in LFCM System at Karlsruhe, FRG (from Weisenburger 1979)

performance characteristics of all such devices to be quite similar. Table 4.1 presents experimental aerosol DFs characterizing both types of scrubbers. The performance similarities previously referred to are not immediately apparent from the data presented in this table. However, the reason for variances in the data is due to the differences in nature of the aerosols evolved during the various tests. The large differences in overall venturi scrubber efficiencies between the PSCM-7 and PSCM-8 test can be explained by the large differences in the size distributions of aerosols generated during the tests. Table 3.3 showed that during the PSCM-7 test, only ~10% of the mass of melter-generated aerosols were greater than 1 μm ; however, during PSCM-8, 50% of the melter aerosols were greater than 1 μm . As a result, overall DFs for PSCM-8 were much greater than those recorded during PSCM-7, as shown in Table 4.1. The difference between venturi and SBS scrubbing efficiencies that occurred during WVNS tests PSCM-9 and PSCM-15 can similarly be explained by again referring to Table 3.3. Scrubbing efficiencies for cesium aerosols, which are predominantly sub-micron, should not be so strongly influenced by the test-dependent melter behavior. This is also found to be true as is shown in the Table 4.1.

Pacific Northwest Laboratory has also examined the nature of aerosols capable of penetrating low efficiency quench scrubbers. Figure 4.5 presents size distribution data involving aerosols exiting a ejector-venturi and an SBS, respectively. The data show that both types of quench scrubbers are efficient in removing aerosols larger than 1 micron generated by a gross entrainment mechanism, but do little to remove submicron airborne matter. Therefore, those process-related factors that act only to increase gross entrainment will not substantially influence or affect off-gas characteristics downstream of the initial quench scrubber. Such conditions can result from short-term overfeeding conditions or through intentional use of force-glass convective processes.

The impact of steam collapse on quench scrubber efficiency has been tested for the SBS. The PSCM-19 test was conducted using air film cooler which so diluted the LFCM exhaust that the SBS was condensing very little melter-generated steam. However, the aerosol performance of the SBS was quite comparable to previous established values as can be seen by comparing the data in Table 4.1.

TABLE 4.1. Quench Scrubber Experimental Aerosol DFs

Element	Aerosol DF						
	Ejector-Venturi				SBS		
	PSCM-7	PSCM-8	PSCM-9	PSCM-17	PSCM-15	PSCM-16	PSCM-19
Al	81	5,900	11	1,400	590	1,400	1,100
B	5.2	6,000	3.3	810	4,200	44,000	1,300
Ba	--	--	170	--	40	450	460
Ca	90	79	1.5	87	47	480	540
Cd	19	14	33	--	--	--	--
Cl	--	37	640	190	--	--	--
Cr	32	100	7.3	--	51	41	60
Cs	18	11	7.1	5.8	5.9	9.5	6
Cu	20	260	7.9	--	1.2	--	--
F	11	--	--	--	--	--	--
Fe	260	3,600	250	--	3,700	11,000	2,700
I	--	--	--	1.4	--	--	--
La	52	800	71	--	3,700	650	1,000
Li	23	63	7.6	--	81	56	18
Mg	--	220	58	--	1,200	530	--
Mn	470	1,500	26	--	1,200	42	1,300
Na	20	33	7.5	60	19	33	23
Nd	140	--	12	--	4,700	590	1,500
Ni	120	150	1.8	--	--	--	690
Pb	12	13	8.4	--	--	--	--
Ru	--	--	38	--	50	4,200	16
S	7.7	75	8.2	44	30	44	--
Sb	23	36	16	--	13	--	--
Se	7.9	3	3.3	--	21	19	--
Si	180	10,000	31	2,900	62,000	38,000	8,000
Sr	9.1	360	--	360	9,800	1,300	1,300
Te	14	13	19	--	6	690	--
Ti	13	--	95	--	2,300	--	120
Zn	23	900	11	--	--	--	--
Zr	36	--	9.1	--	740	160	850
TOTAL	9	54	6	36	32	28	29

-- = Data below detection limit.

FIGURE 4.5. Size Distribution of Aerosols Exiting the Primary Scrubber

The performance of the plate column scrubber shown in Figure 4.4 is described by Weisenburger et al. 1979. This device is operated with the pilot-scale LFCM at Karlsruhe, FRG. The overall DF on feed oxides averaged about 9. The average DF for Cs was only about 3 across the scrubber. The average DF for ruthenium was 16 during runs with nitrate-containing feed (3.7 HNO_3), and was about 6 during runs with denitrated feed. The concentration of Ru entering the plate scrubber is about three times higher in feed that contains nitrates than in denitrated feed. The ejector-venturi and submerged bed scrubbers studied in connection with the PSCM at PNL have exhibited substantially better performance

than this plate column at Karlsruhe. The differences in performance should be evaluated in terms of the design and operational characteristics of each scrubbing device.

4.1.2 Radioactive Gas Collection Performance of Primary Scrubbers

The elements of particular importance with regard to LFCM gaseous emission are tritium, ruthenium and iodine. The major chemical forms responsible for the gaseous emission of these elements are HTO , RuO_4 , and I_2 , respectively. Process control of LFCM tritium emissions, if required, is limited to condensation and/or exchange. Use of cooling via air injection would reduce condensation efficiency because of dilution. However, in dealing with LFCM-generated tritium, a low-level waste stream at least as large as the original high-level liquid waste volume (HLLW) is produced. In order to carry out effective exchange, the scrubbing liquid of the quench scrubber would have to be continually refreshed with nonprocess water, consequently creating the additional and unmanageably large waste stream. As a result, it is prudent to try to eliminate tritiated waste from the liquid waste stream before it is fed to an LFCM.

Gaseous Ru off-gas emissions are important only in highly oxidizing feeds. Under these conditions, more than 90% of the Ru lost from an LFCM is in the gaseous state. However, quench scrubber DFs for gaseous Ru are quite still high. No evidence for Ru gaseous penetration of quench scrubbers (either SBS or ejector-venturi) has been found at PNL. Using the analytical detection limit associated with gaseous samples generated during LFCM processing of oxidizing feed, the quench scrubber DF for gaseous Ru has been estimated to be 400.

This lower limit to Ru DF assumes low concentrations of Ru in the scrub liquor. If Ru concentrations build up in a highly acidic, nitrated solution, Ru revolatilization may occur. This is an important consideration if evaporative concentration of the scrub liquor is part of the recycle process.

Gaseous evolution of halogens is to be expected from LFCMs irrespective of redox condition of the feed. The processing of oxidizing feeds will strongly promote elemental losses of these elements. In particular, complete melter volatilization of iodine in the feed as I_2 is expected under these conditions.

Although data on quench scrubber DFs for I_2 are limited, the study that was conducted on an oxidizing WVNS feed (PSCM-9) suggest a very minimal scrubbing efficiency (DF ~1) for this gaseous effluent. Consequently, if the ^{129}I content of LFCM feed requires control, very little credit can be given to the quench scrubber if I_2 is strongly evolved during LFCM processing.

4.2 HIGH-EFFICIENCY AEROSOL SCRUBBERS

As discussed in Section 3.0, a large portion of melter-emitted aerosols are less than 1 micron. After passing through the primary scrubber, it is generally not practical to collect these emissions solely with high efficiency particulate air (HEPA) filters because frequent changeout of these filters would be required. Instead, these aerosols can be removed with low-maintenance devices. The discussion here will focus on two such devices: the Hydro-Sonic® scrubber (HSS) and a filter known as the high efficiency mist eliminator (HEME). These units are being considered for use at Hanford and West Valley, and are in the DWPF design.

The HSS is an air- or steam-aspirated wet scrubber that collects aerosols using a supersonic nozzle to efficiently atomize water by injecting water into the wake of an expanding free jet (see Figure 4.6). A brochure^(a) describes the phenomenon as follows: dirty gas is driven through a free-jet nozzle fitted with a water-injection ring where water is injected on to the driven gas stream. Turbulent mixing occurs as the free jet expands, causing capture of particulates in the very fine submicron sizes.

The HEME (Figure 4.7) is configured so it can be irrigated and drained and is most effective for collection of soluble mists or fumes. HEMEs were originally developed by Brink (1964) for removal of acid or caustic fumes, and are available today from several domestic vendors with either fiberglass or polypropylene batt. These filter fibers are designed for collection of submicron aerosols. In LFCM service, much of the airborne material is not water-soluble, so the washability of the HEME is not certain. If these filters cannot be washed effectively, they would require frequent replacement, which is a

(a) From Hydro-Sonic® brochure, Lone Star Steel Company, Dallas, Texas.

FIGURE 4.6. Principle of Operation of Hydro-Sonic® Scrubber, Adapted From Lone Star Steel Co. Brochure

FIGURE 4.7. Schematic of High-Efficiency Mist Eliminator Used in PNLs PSCM Off-Gas System

negative factor in the use of the HEME itself. HEPA filters, for which remote-replacement housing designs already exist, could be used instead. This concern has been recognized by DWPF designers who have located the HEME after the HSS; in this role, the HEME serves to collect mists.

The following sections describe the aerosol efficiency of the HSS and the HEME.

4.2.1 Hydro-Sonic® Aerosol Scrubbing Efficiency

LFCM off-gas testing of Hydro-Sonic® scrubbers has been almost exclusively conducted by SRL, (Colvin 1983) although PNL has had some limited experience. SRL off-gas design provides for two cascaded hydrosonic devices directly downstream of the LFCM ejector-venturi ejector quench scrubber. Consequently, most of the LFCM scrubbing performance data associated with this device involves the tandem, cascaded system which is designed to meet a DWPF-required DF of 50 for Cs aerosols. PNL performance data was obtained from a single unit located downstream of the LFCM quench scrubber. Representative data obtained from both laboratories is given in Table 4.2. Interlaboratory comparison of single-stage hydrosonic DFs agree quite well. However, the important comparison to be made is between single and dual stage operational performance data. The efficiency of the first scrubber does not impair or degrade the Cs DF or the total DF of the second. Indeed, the first unit appears to slightly improve the performance of the second for both the Cs DF and the total DF.

The data presented above suggest that Hydro-Sonic® scrubbers are well suited for process control of submicron aerosols generated by LFCMs. The devices are not passive but require little more than steam and/or compressed-air service.

4.2.2 HEME Aerosol Scrubbing Efficiency

High efficiency mist eliminators are currently being tested as deep-bed, high-efficiency washable filters in LFCM off-gas processing systems. The main virtues of employing HEMEs for this purpose are that they are passive, renewable, and highly efficient. However, because the main purpose of an HEME in LFCM applications is to remove semivolatile (Cs) submicron aerosols, a great deal of attention must be given to conditions of off-gas or HEME operation.

TABLE 4.2. Hydro-Sonic® DFs

Element	SRL		PNL
	Cascaded	Single	
Al	--	--	--
B	--	--	23
Ba	--	--	4.7
Ca	--	--	1.3
Cr	--	--	6.6
Cs	61	7.2	4.9
Fe	--	--	9.2
Li	--	--	6.1
Mg	--	--	1
Mn	25	38.6	17
Na	61	8.9	6.1
Sr	3	5.2	5
Zr	--	--	3.2
Total	47	9.0	12

-- = Data below detection limit.

Specifically, the dew point of the filtered off-gas stream must be kept significantly below operating off-gas system temperatures. If this condition is not met, condensation will occur on the HEME element. The resulting water film will carry soluble semivolatiles through the filter, effectively penetrating the barrier designed to stop them, and will subsequently be reentrained by the exhausting gases. Table 4.3 compares performance data collected under both wet and dry conditions.

The Savannah River Laboratory routinely uses a spray wash with their HEME in LFCM off-gas processing applications. The performance of their HEME during the 90-day LFCM test is also included in Table 4.3 for comparison. These SRL DFs are not necessarily directly comparable to the PNL data in that two cascaded hydrosonic scrubbers were used to pretreat the off-gas stream before HEME filtration. Because Hydro-Sonic® scrubber operation is based upon altering (increasing) the aerosol size distributions, the pretreatment step could serve

TABLE 4.3. HEME Aerosol DFs

Element	PNL		SRL
	Dry	Wet	
Al	--	10	--
B	120	42	--
Ba	3	15	--
Ca	5	14	--
Ci	36	11	--
Cs	54	1.2	111
Cu	2	--	--
Fe	9	18	--
K	28	--	--
La	--	17	--
Li	37	11	--
Mg	19	--	--
Mn	--	14	33
Mo	25	--	--
N	50	--	--
Na	47	12	221
Nd	--	--	--
Ni	3	5	
P	47	--	--
Ru	--	8.1	--
S	53	--	--
Sa	--	--	--
Si	--	18	--
Sr	--	14	--
Ti	--	--	--
Zn	5	--	--
Zr	--	24	--
Total	15	2	39

-- = Data below detection limit.

to increase effective HEME DFs and be responsible for the differences in the laboratory data. However, the two sets of data do provide a good general sense of the usefulness of HEMEs for dealing with LFCM submicron aerosols.

Semivolatile penetration of HEMEs through aqueous solution transport is convincingly illustrated by examining the reentrained matter collected downstream of the wet filtering media. Figures 4.8 and 4.9 present photographs of these aerosols taken under various degrees of magnification using a scanning electron microscope. Although filter loadings preclude statistical size analysis of the aerosols collected, one thing is abundantly clear: essentially all of the collected matter is large, i.e., greater than 1 micron. Particulate matter collected under dry conditions are of course submicron as is shown in Figure 4.10. The composition of typical particles called out in Figures 4.8 and 4.9 are identified in X-ray fluorescence spectra appearing in Figures 4.10 and 4.11. In all cases, it is found that the Cs and Se in the samples are associated with large rod-like fibers. The fibers are crystals that have grown from solutions that are concentrated through the evaporative process on the downstream side of the HEME. Clearly, the purpose of a HEME in an LFCM off-gas system is negated under these wet unit operating conditions.

Wet operation with HEMEs can be effectively accomplished however, if the HEME is washed by design. Filters can be continuously washed or irrigated in a countercurrent direction to the flow. Though operation may increase the pressure drop across the device, it is fully capable of preventing solution penetration of the filter. The once-through wash water, of course, would create another waste stream which would have to be dealt with.

4.3 CONTROL OF NITROGEN OXIDE EMISSIONS

Present day nuclear fuel reprocessing plants use the plutonium and uranium extraction (PUREX) process which involves dissolution of fuel and fission products in nitric acid. High-level radioactive wastes resulting from the PUREX process are therefore present as nitrate salts in aqueous nitric acid solutions. Solidification of these aqueous wastes into nonsoluble products typically involves heating the wastes to temperatures above the decomposition temperature

AREA #1

AREA #2

AREA #3

AREA #4

AREA #5

FIGURE 4.8. Aerosols Exiting the Hydro-Sonic® Scrubber

FIGURE 4.9. Aerosols Exiting the High-Efficiency Mist Eliminator

FIGURE 4.10. X-Ray Fluorescence Spectra of Selected (Hydro-Sonic®) Particles Appearing in Figure 4.8

FIGURE 4.11. X-Ray Fluorescence Spectra of Selected (HEME) Particles Appearing in Figure 4.9

of nitrate salts, resulting in gaseous evolution of nitrogen oxides. In order to meet emission limits for nitrogen oxides, an abatement process may be required.

Nitrogen oxides present as NO and NO₂ represent potentially important pollutants; the two oxides together are referred to as NO_x. NO₂ is the more reactive, and if NO did not oxidize to NO₂, NO would probably not be considered an important pollutant. However, NO oxidizes at an appreciable rate, and under normal circumstances becomes almost completely converted to NO₂. Thus, the potential NO₂ concentration is the sum of NO and NO₂, and the sum of these two species, NO_x, is commonly used as a measure of the NO₂ concentration in evaluations pollutant emissions.

This section summarizes information from the literature on: 1) the sources of NO_x from the LFCM process, 2) properties of the important NO_x compounds, and 3) control processes for airborne NO_x. Benefits and limitations of available control technologies are discussed.

4.3.1 Sources of Nitrogen Oxides

The primary sources of nitrogen oxide resulting from the LFCM process are the melter and, if used, the nitric acid decomposer. The quantity of NO_x emitted depends on waste NO₃⁻ concentrations treated, and on the kind of acid destruction process used. In the melter, nitric acid is vaporized or converted to NO_x and nitrate salts are converted to NO_x. Analyses of off gas from melters operated at PNL (see Section 3.0) show that when the slurry feed contains reductants, such as formic acid, the nitric acid/nitrate salt reaction products are NO and NO₂. However, if the feed and plenum atmospheres are oxidizing, only NO₂ is present. Because of its low vapor pressure, any HNO₃ evolved will condense in the wet aerosol-scrubbing equipment, but NO_x gases will not necessarily be captured by devices such as the ejector-venturi and the SBS because these are not specifically designed for gas contacting.

A nitric acid reducer is often used to dispose of, or limit the buildup of nitric acid in the high-level waste evaporator. Reductants that have been studied for this purpose include formic acid, formaldehyde, and sugar. The nitric acid reduced in this manner is evolved as oxides of nitrogen.

4.3.2 Properties of Nitrogen Oxide Compounds

A wide variety of nitrogen oxides have been characterized, corresponding to oxidation states of nitrogen from +1 to +5. Those oxide species that must be controlled are briefly discussed based on information available in Jolly (1964) and Yaws and Hopper (1974).

Nitric oxide, NO, is only slightly soluble in water and therefore cannot be efficiently removed in ordinary aqueous scrubbers. The most important property of NO is its homogeneous reaction with oxygen to form NO₂. The equilibrium for oxidation of NO strongly favors the production of NO₂ at lower temperatures so that below 150°C almost all nitric oxide would combine with oxygen present.

In the gaseous and liquid states, the two oxides NO₂ and N₂O₄ always co-exist. Nitrogen dioxide (NO₂) is the brown gas that causes the colored plume issuing from nitric acid plants and other operations that emit appreciable quantities of NO_x. Dinitrogen tetroxide (N₂O₄) is colorless. Little data on the solubility of either NO₂ or N₂O₄ in water are available because these gases react with water.

4.3.3 Control Methods for NO_x

The control methods considered viable for LFCM applications are aqueous absorption and catalytic conversion. In absorption, airborne NO_x is contacted with and thus physically absorbed by liquids. Where water or nitric acid are used as the scrubbing agent, nitric acid may be reclaimed as a product which can be reused "in plant." If there is no reclamation, liquid waste is typically generated, and a gaseous effluent becomes a liquid waste. Conversion of NO_x involves controlled chemical conversion. The conversion of NO_x to form N₂ and other innocuous gases requires a reactant and acid is not recovered. Equipment costs, however, may be appreciably lower for conversion process than for absorption processes.

4.3.3.1 Absorption

The absorption of nitrogen oxides into aqueous solutions is a process that has been used extensively in industrial applications and has received a great amount of technical analysis. However, because of the complexity of the chemical system involved, there are differences of opinion as to the absorption mechanisms. Mechanisms are discussed by Wendel and Pigford (1955) and more recently by Counce (1984).

Based on a review of NO_x scrubbing by aqueous solutions, the following conclusions and summary statements can be made:

- Nitrogen oxides are difficult to remove by aqueous scrubbing, particularly at low concentrations. Very few tests have demonstrated more than 90% removal of NO_x , with most reported results ranging from 20% to 70% removal (Peters 1955).
- The mechanisms that lead to NO_x absorption are complex and not yet fully understood. A satisfactory model for predicting absorption may have to include up to eight mechanisms (Andrew and Hanson 1961).
- The design of nitric acid plants is certainly an established technology, and available design calculations, e.g., as discussed by Sherwood and Pigford (1952), have apparently been sufficient to guide the design of NO absorption towers. The fact that the complexities in the mechanisms has not prevented adequate designs is attributed to two factors: first, considerable empiricism has no doubt been used in designs, and second, at high NO concentrations, one or two mechanisms control the absorption rate. It should be noted that nitric acid plants have a tail gas problem with residual NO_x which is not absorbed in the acid towers. This tail gas problem is similar to the problem arising from waste solidification.
- Sodium hydroxide solutions are not appreciably better than water or dilute acid in removing NO_x (Peters 1955).
- Scrubbing with any agent except plain water or nitric acid leads to generation of liquid wastes, and in effect, the air pollution problem may be transformed into a water pollution problem.

- Experimental test data would be needed to develop an adequate design for an NO_x scrubber. While models for NO_x absorption are available, the state of the technology is not far enough advanced to permit confident design of an absorber based solely on theory. The required experimental data could come from experience on similar equipment or from bench-scale laboratory tests. Counce (1984) indicates that the recently introduced structured packings, such as wire gauze and chevron baffle types, may offer significant advantages over traditional dump-packings in the capture of NO_x fumes at low, but troublesome concentrations. Such low concentrations may be encountered in the LFCM off-gas system.

4.3.3.2 Conversion

Control of NO_x by conversion involves the addition of a chemical to the gas which reacts with NO and NO_2 to form innocuous products. Three methods of available conversion are thermal reduction with a hydrocarbon fuel, catalytic reduction with a hydrocarbon fuel, and catalytic reduction with ammonia.

Thermal conversion of NO_x with propane or natural gas requires approximately 8% combustibles and temperatures of 980 to 1100°C. Outlet concentrations of 300 to 650 ppm NO_x can be achieved, but fuel costs become high because all the oxygen must be consumed before NO_x can be reduced.

Catalytic reduction of NO_x takes place in the presence of noble metals at temperatures of 650 to 750°C. The lower operating temperature requires less fuel, but is at the upper operating temperature limit of the catalyst. Because of this limit, the performance is less predictable and catalyst life would be expected to be short.

Catalytic reduction with ammonia is promoted with zeolite catalysts, and occurs at low temperatures. The process has been developed by Mays and Schwab (1975). Conversion is quite high with inlet concentrations of 20,000 to 60,000 ppm, but drops quickly at higher concentrations. An important safety concern of this process is the potential for formation of NH_4NO_3 , which is an explosive. Of the conversion processes, only the ammonia reduction system appears to have potential.

If NO_x abatement is necessary, then a selection must be made between what appear to be the most viable processes for LFCM application: aqueous absorption or ammonia conversion. Either process will likely deliver the required efficiency, if properly designed. The conversion process has the fundamental advantage of not creating a secondary waste stream. However, it has the disadvantage of requiring high temperatures, and the potentially explosive compound ammonium nitrate can be formed in the reactor. The aqueous absorption process has the advantage of being able to remove gases other than just NO_x , in particular halogens that may interfere with a silver-based iodine capture system. Additionally, a second aqueous scrubber can serve to back up the LFCM primary scrubber.

4.4 RADIOACTIVE GASES

The principle radionuclides in high-level waste that can exist as gases are tritium, ruthenium-103 and -106, and iodine-129 and -131. Experimental information presented in Section 3.0 showed that iodine will probably be 100% volatilized from the melter, as will 10 to 50% of the ruthenium. Tritium will also be completely volatilized during LFCM operations. This section presents information obtained primarily from the literature on the behavior of tritium, ruthenium and iodine in radioactive off-gas systems and methods for removal of their gaseous forms.

4.4.1 Tritium

Because of waste pretreatment steps such as evaporation and sludge washing, tritium will probably not even reach the melter, and thus the LFCM off-gas system. Any tritium will probably be in a vessel vent system, or could go to low-level liquid waste. Whether in a vent or off-gas system, removal may be required prior to stack discharge of the vent or process gases.

The most likely form of volatile tritium is HTO ; this compound behaves chemically like water. Removal of airborne HTO (beyond levels attainable with typical process equipment such as condensers) requires drying techniques involving cryogenic traps or molecular sieve adsorbents. There has been limited development of this technology on the scale needed for LFCM process off-gas systems (100-300 cfm), as most studies to date involve either bench

scale development or application to relatively low air-volume systems such as glove boxes. A system has been in use at the Mound Facility (Lamberger and Gibbs 1978) involving molecular sieve dryer beds. This tritium removal system is near the size needed for LFCM use, having a capacity of 60 cfm. However a vessel vent system, which is likely to contain most of the tritium, could have air volumes on the order of several thousands of cfm.

4.4.2 Ruthenium

Most of the literature on high-temperature volatilization of Ru deals with various calcination processes. This process has been utilized for radioactive waste fixation for many years in both Europe and the U.S. Only limited literature is available on Ru volatilization from the LFCM process. A review of some of the literature on Ru behavior during calcination is given followed by a discussion of LFCM Ru volatilization studies. Finally, methods for removal of gaseous Ru are reviewed and discussed.

4.4.2.1 Properties of Gaseous Ruthenium Effluents

Christian (1976) has extensively surveyed the Ru control literature and summarizes his experience gained during calcination tests as follows. During high temperature waste solidification of neutral or basic wastes containing reducing agents, no significant volatilization of Ru occurs, even with nitrates present. When nitric acid wastes are solidified at high temperatures, significant quantities of Ru can volatilize. This assessment concurs with the discussion of PNL data in Section 3.0 obtained from LFCM operation.

The principal species responsible for volatilization at calcination temperatures is unknown. Evidence exists that a species other than RuO_4 may form, probably a nitrosyl ruthenium gas complex. With fluoride present in the nitric acid waste, a highly volatile oxyfluoride or nitrosyl fluoride may form. In the presence of O_2 , RuO_4 becomes increasingly important and is a thermodynamically stable gas species above 600°C .

The behavior of Ru in an LFCM has been studied by Klein et al (1982) in a laboratory unit. The off-gas purification system consisted of a packed bed dust scrubber, a specific Ru filter, an ejector-venturi scrubber, and a condenser. The feed was simulated low-enriched waste concentration solution and

contained 6.3 g/L of $\text{RuNO}(\text{NO}_3)_3$ as a radioactive tracer. The level of nitric acid in the feed solution was not given. The volatility of Ru depended on factors such as feed rate, degree of glass pool coverage and air sparging flow rate (inleakage). With a liquid flowrate of 0.14 L/hr and a sparge rate of 90 L/hr, the volatility ranged from 15 to 20% (melter DF of 6.6 to 5). An increase in liquid feed rate from 0.14 to 0.17 L/hr and a decrease of the sparging rate from 90 to 60 L/hr reduced volatility to 3 to 7%. The fraction of Ru in a volatile form that escaped the melter was in the range of 1 to 10%. This volatile Ru was trapped by a condenser which immediately followed the melter. The Ru melter DF was dependent on the chemical species of Ru in the feed. With $\text{RuNO}(\text{NO}_3)_x$ the mean DF was 13, and with RuO_2 the DF was as high as 40.

4.4.2.2 Methods for Removal of Ruthenium from Gas Streams

Various sorbent beds have been proposed for removal of volatile ruthenium. Hansen et al. (1958) and Rhodes (1959) performed early work on Ru sorption onto silica gel and obtained DFs of 1000. Newby and Barnes (1975) evaluated a number of Ru adsorber materials for a fluidized bed system which calcined 6M HNO_3 waste solutions. Silica gel, hydrous zirconium oxide, and ferric oxide were found to provide DFs of 1000 or greater. Silica gel was selected for use due to its regenerability and low temperature operation.

Klein et al. (1982) studied volatilization and gas phase removal of Ru during calcination of nitric acid solutions. In a series of experiments, ruthenium was introduced to the gas stream in different ways as shown in Figure 4.12. The RuO_4 generator utilizes a reaction of RuCl_3 with KIO_4 in a sulfuric acid solvent to produce RuO_4 gas. When RuO_4 is mixed with NO_x vapors from the calciner (Case III), it was determined that a gas phase reaction occurs between RuO_4 and NO_x to form a less volatile compound (perhaps a Ru nitrosyl complex).

When RuO_4 in dry air was fed to a silica gel sorber (Case I), a DF of greater than 1000 was obtained with a silica gel absorption capacity of 1 mg Ru/g sorbent. The bed temperature was 20°C and the inlet RuO_4 concentration was 100 mg/m³. The absorption capacity was found to increase linearly with gaseous RuO_4 concentration and decrease with adsorption temperature thus following the Arrhenius model with a heat of adsorption equal to 29 kJ/mole.

Cases I and II RuO_4 With Dry or Moist Air

Case III RuO_4 Fed at Outlet of Calciner and Mixed With NO_x

FIGURE 4.12. Description of the Experimental System Used in Klein et al. (1982)

Adsorption of RuO_4 on silica gel in a moist carrier gas (Case II) was much less efficient than in the dry gas. Dew points from 15-80°C were studied. The adsorbent bed must work at a temperature higher than the dew point to avoid condensation. The combined influences of higher bed temperature (50-100°C) and competition of adsorption sites between RuO_4 and H_2O resulted in rapid bed saturation and a DF which fell to 1.0 after a brief operating period.

When RuO_4 was mixed with calciner emissions (NO_x and H_2O , see Case III), DFs higher than 100 were obtained when the bed was held at 100°C. No bed saturation was observed during the course of the test.

In another set of experiments, Klein et al. (1982) studied calcination of 3.5 M nitric acid containing ruthenium nitrosyl nitrate $[\text{RuNO}(\text{NO}_3)_x\text{OH}_3]$ spiked at 50 mg/L. It was found that adsorbers did not work when placed after a condenser which treated calciner effluents; evidently only Ru aerosols were present at the condenser discharge. Adsorbents performed only when placed directly at the calciner exit. Two types of silica gel, two types of molecular sieves, and $\text{SiO}_2/\text{Al}_2\text{O}_3$ with ferric-oxide/chromium oxide deposits were tested. For all adsorbents, similar DFs were found in the range of 10 to 100. Capacities were

not determined because none of the beds saturated. The molecular sieve materials (Zeolon® 900H and UC13X) were more resistant to water condensation than the silica gels. Klein et al. state that on the basis of their tests, the molecular sieve materials are preferable over the silica gels for Ru adsorption. Several catalysts were tested by Klein et al. for removal of volatile ruthenium: metal oxides on a Si/Al support; Zeolon® 900H impregnated with RuO_2 , Fe_2O_3 , or Cr_2O_3 ; and various commercial catalysts. The optimum bed temperature was 300°C for most catalysts. DFs were in the range of 2 to 10 for metal oxide and Zeolon® 900H catalysts, and 10 to 100 for the commercial catalysts.

The early work performed by Rhodes (1959) and also reported by Newby and Barnes (1975) showed that silica gel is effective for ruthenium capture under conditions where its gas concentration is high ($>1 \text{ mg/m}^3$) and the gas stream is dry. However, Cains and Yewer (1983) have found that once loaded, silica gel beds have a tendency to desorb Ru when subjected to process gas with reduced Ru concentration. This would occur, for example, during down-time periods or during process feed fluctuations. The loss of Ru is attributed to desorption of physisorbed species, perhaps RuO_4 . Additionally, the DF performance of silica gel is found by these workers to suffer markedly at Ru concentrations of less than 0.5 mg/m^3 . It would appear that silica gel is not suitable for LFCM off-gas system applications since down-time is anticipated as well as low Ru gas concentrations.

Cains and Yewer (1984) have performed screening tests on alternate capture media, focusing on transition metal catalysts. The intent is catalysis of the reaction of RuO_4 to the more stable, solid form RuO_2 . In separate tests, they studied oxides of Fe, Ni, V, Cr, Cu, Zn, Mo, Co, and Mn doped individually onto alumina supports and also silicated iron oxide, and Ru metal on alumina support. A packed bed of 5.8 cm diameter by 50 cm long was operated at 350°C for the tests. A calciner pot was used to volatilize Ru at 400°C from a solution of 10 mg/L Ru (as a nitrosylruthenium complex) and 8M nitric acid. The most promising catalysts were zinc oxide, ruthenium metal, nickel (II) oxide, and

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chromium (III) oxide on alumina supports. Decontamination factors for Ru ranged from 400 to 2500 for these candidates and suitable retention characteristics were indicated. Because of the preliminary nature of Cain and Yewer's study, it appears that further investigation is needed before these materials can be deployed in LFCM off-gas systems.

4.4.3 Iodine

A discussion of volatile I_2 emissions from calcination or vitrification processes has not been found in the literature. This may be due, in part, to the fact that nearly all iodine is out-gassed in reprocessing steps that occur prior to calcination or vitrification. The only known references for volatile iodine control pertain to off gas from dissolver solutions.

From the standpoint of volatile iodine recovery, the differences between calciner/vitrification effluents and dissolver effluents are:

- dissolver off gas is likely to be more concentrated in iodine than calciner/vitrification off gas
- dissolver off gas may contain methyl iodide (CH_3I) as well as I_2 whereas calciner/vitrification off gas is likely to contain only I_2 due to the instability of other species at the high temperature of solidification processes.

Holladay (1979) and Burger and Scheele (1983) have extensively reviewed the literature on removal of iodine from off gases, specifically these processes: Iodox wet scrubbing (hyperazeotropic HNO_3), mercuric nitrate-nitric acid wet scrubbing, sorption on charcoal, metal exchanged zeolites, sorption on $AgNO_3$ impregnated silicic acid, sorption on Ag- and Pb-exchanged mordenites, and sorption on macroreticular resins. The first two processes involve wet scrubbing whereas the latter methods involve use of solid sorbents. Specific wet scrubbing for iodine may not be practical for most LFCM off-gas systems because of process complexities, the need for special reagents, and copious liquid effluent generation. Thus, the solid sorption techniques will be emphasized.

Holladay's review describes activated charcoal as an effective sorbent for I_2 capture over a wide range of I_2 gas concentrations, from as low as $10^{-3}g$

I_2/m^3 up to 10^3 mg I_2/m^3 . Some of the disadvantages of charcoal are: it can ignite at temperatures of 200°C , it desorbs iodine at high temperatures, and it is deleteriously affected by NO_x gases (with possible formation of explosive compounds). Though macroreticular resins such as Amberlite XAD-4 have shown to be effective in removing I_2 , they, like charcoal, can readily release I_2 , are combustible, and also have questionable radiation stability.

Silver exchanged zeolites (AgX) have been found effective for I_2 capture from off gases. Holladay describes work by Staples (1976) where I_2 adsorption capacity decreased in the presence of 2% NO_2 . Experimental work indicates that loading capacities for AgX range from 6 to 140 mg I_2/g -sorbent and DFs range from 10^2 to 10^5 . Typical operating conditions were 10-500 mg- I_2/m^3 inlet gas concentration, 0 to 2% relative humidity and feed gas temperatures of 100- 200°C . The negative effect on absorption capacity experienced when AgX was subjected to 2% NO_2 may preclude this sorbent materials for use in systems with significant NO_2 concentrations. However, an attractive feature of the AgX sorbent is its ability to remove I_2 from the gases to as low as 10^{-10} mg- I_2/m^3 .

Another silver-loaded substrate is mordenite (AgZ) which is prepared from the synthetic sodium mordenite Zeolon® and is more resistant to acidic environments than AgX. When heated in the presence of H_2 , reduced silver is formed on the catalyst and the material is then designated Ag°Z . Ag°Z demonstrates higher loading capacity than AgZ (Burger and Scheele 1983).

Holladay's (1979) review of work by Slansky indicates that Ag°Z is superior to AgX because of greater acid stability, higher loading capacity, and higher removal efficiency. Testing with mordenite doped with reduced silver (obtained by H_2 pretreatment) is summarized as follows. With a simulated dissolver off gas stream of 6% H_2O , 2% NO_2 and 2% NO and a bed temperature of 150°C , I_2 DFs of 10^3 and 10^4 were reported at loading capacities of about 120 mg I_2/g sorbent. Burger and Scheele (1983) report that the DF decreases when the I_2 loading exceeds 30 to 40% of the theoretical capacity which is 200 mg I/g AgZ.

Amorphous silica impregnated with AgNO_3 was developed in the FRG and has been known by the commercial name of AC-6120. The material is used much like AgZ or AgX and contains 7 to 12 wt% silver. Beds can be operated at 110- 160°C . Burger and Scheele (1983) cite work by Furrer, Kaempfer, and Wilhelm

(1982) in which DFs greater than 10^4 were obtained. Iodine loadings of 95% silver utilization were achieved and 60% silver utilization was achieved before DFs dropped below 10^5 . The process is compatible with NO_x in the off gas.

4.5 FINAL FILTRATION

High efficiency particulate air (HEPA) filters can be used as the final treatment step in an LFCM off gas system. Of all the filtration components, HEPA filters are the most aggressive toward submicron capture. With submicron removal devices prior to the HEPA filters (Hydro-Sonic® scrubber and/or HEME), it is anticipated that a majority of the melter-emitted aerosols will be removed by the time gas reaches these final filters. Their inclusion in an off-gas system however, may be necessary in order to assure thorough decontamination prior to discharge to the stack. Tests of HEPA performance have not been carried out during LFCM operation so the information presented here is from the literature of HEPA application in related nuclear service.

As with the HEME, the principal submicron capture mechanism is brownian diffusion. Filtration efficiency varies strongly with particle size and is a minimum for sizes around 0.4-0.7 microns (Fullwood and Mendoza 1979). Table 4.4 shows penetration versus particle size through a bank of HEPA filters in series. The DF (inverse of penetration) does not drop sharply as particles progress from one stage to the next, a consequence of the controlling diffusion mechanism.

Elder et al. (1980) have performed in-place tests on tandem HEPA filters in a large system (20,000 cfm). They used a sonic nozzle generator which resulted in a stream of particles with $0.17 \pm 0.04 \mu\text{m}$ median diameter. The first stage of the HEPA filters exhibited DFs of approximate 8×10^3 to 5×10^4 ; the second stage had DFs of between 5×10^3 and 2×10^4 . Combined DF for the tandem system was around 10^8 . The scatter in their data did not permit evaluation of DF vs. particle size; however, the data did indicate a diminishing DF below 0.15 microns. Overall, the results of Gonzales and Elder are in agreement: very high particulate DFs are expected from tandem HEPA filters.

It is evident that HEPA filters are an effective final cleaning step for aerosols, but there have been no investigations on the lifetimes of these

TABLE 4.4. Fractional Penetration^(a) of Dry-Process Polydisperse Aerosol Through Various HEPA Filter Stages^(b)

Particle Size Range, μm	Reference Fractional Distribution	HEPA 1 $\times 10^{-6}$	HEPA 2 $\times 10^{-6}$
<0.12	--	36 $\pm$ 36	200 $\pm$ 220
0.12 - 0.22	0.0001	54 $\pm$ 50	82 $\pm$ 31
0.22 - 0.44	0.002	71 $\pm$ 59	92 $\pm$ 24
0.44 - 0.96	0.038	64 $\pm$ 57	126 $\pm$ 82
0.96 - 1.54	0.10	39 $\pm$ 33	24 $\pm$ 19
>1.54	0.86	30 $\pm$ 30	4.2 $\pm$ 2

(a) DF is the inverse of these fractional penetrations.

(b) Source: Gonzales 1976.

filters specifically for LFCM off-gas systems. This is an important aspect in system design because HEPA filters, which will likely be required in order to assure compliance with stringent environmental release limits, must be capable of a reasonable lifetime. Upstream air-cleaning equipment must be designed to reduce the aerosol loading to a level that is tolerable for HEPA filters.

Barring non-routine failures, filters are generally replaced when accumulated solids cause pressure drop across the filter to exceed a specified limit. The effect of dust loading on pressure drop is influenced by air flow rate through the filter, type of aerosol, and the area of the filter media. First and Rudnick (1980) relate these factors by the following equation which is based on D'Arcy's Law:

$$H = K_1 \mu \frac{Q}{A} + K_2 \mu \frac{QM}{A^2}$$

where H = pressure drop across filter, Pa
 k_1 = resistance coefficient for clean filter paper, m^{-1}
 k_2 = specific resistance coefficient for dust deposit, m/kg
 Q = volumetric flow rate through filter, m^3/sec
 A = area of filter paper, m^2
 μ = air viscosity, $kg/msec$
 M = the mass of dust collected by the filter, kg .

The first term represents the loss associated with the clean filter (which is generally specified by the manufacturer), whereas the second term is the resistance due to accumulation of dust.

It is difficult to obtain lifetime data on HEPA filters by directly simulating their operation in a test LFCM system because of the long periods likely to be needed to load a HEPA located downstream of aerosol scrubbing equipment. The test could be accelerated by HEPA placement upstream of this equipment but this would be misleading because the aerosol size distribution (and hence k_2) would not be representative of actual service. Therefore, the pressure drop equation above could be used to correlate data obtained from scaled-down equipment tests and thus predict the performance of a full-scale system. In particular, tests need to be designed to derive k_2 for a representative, melter-generated aerosol distribution using a HEPA filter media of interest.

5.0 DESIGN CONSIDERATIONS OF AN OFF-GAS SYSTEM

5.1 ELEMENTS OF AN OFF-GAS SYSTEM DESIGN

Design of a vitrification system for a specific waste composition has historically required extensive testing of feed formulations and melter performance. Development of this technology has progressed to the point that it is now possible to predict the approximate composition and behavior of melter off-gas for certain operating conditions. Given a melter feed composition and flowrate, appropriate treatment equipment can be approximately sized to meet emission limitations. Preliminary system design provides a basis for comparison of candidate treatment systems, and an estimate of total system efficiency.

Melter technology can be applied to high-level liquid wastes of diverse compositions, resulting in a range of system performance requirements. Several features are common to all systems, including the need to collect nearly all particulate material generated, and to maintain constant vacuum in the melter. Systems differ primarily in the quantity and species of hazardous and radioactive gases requiring control. Equipment tested for particulate scrubbing has demonstrated wide flexibility in collecting particulates of various types. Thus the first part of various off-gas system designs will generally look quite similar. Gas removal techniques, however, are usually selective to a single property, and equipment is designed for a narrow range of feed and discharge concentrations.

The general case for off-gas system design, depicted in Figure 5.1, includes unit operations which may be required for various melter feed compositions. A specific case will generally not need one or more of these operations. The sequence of treatment equipment is important to operating efficiency, and thereby influences equipment sizing. Each unit operation is described functionally below, and discussed in more detail in Chapter 4.0.

The first device in the off-gas line is a film cooler. Gases leaving the melter are hot, and carry entrained aerosols and glass particles which tend to accumulate on the pipe wall. Plugging in the off-gas line at the melter gas exit nozzle has been a frequent cause of off-gas system downtime, and can be nearly eliminated by using this device.

FIGURE 5.1. Unit Operations of an Off-Gas System

Melter gases partially cooled by the film cooler are quenched and scrubbed of gross particulate material in the primary scrubber. Candidate equipment includes the venturi scrubber and the SBS. Aerosols are removed in one or more stages of high efficiency particulate removal devices. The Hydro-Sonic® scrubber and the high efficiency mist eliminator can be used individually or in combination for this step. Tritium evolved as HTO is captured by cryogenic or molecular sieve dehumidification. Acid gases including NO_x and SO_x are absorbed in a liquid absorber, usually using water as the absorbent. Gaseous ruthenium is effectively captured on an adsorbent. The gas must be heated before this step. Elemental iodine is adsorbed on a bed of silver mordenite, or other sorbent. Particulate material from the sorption beds is collected on roughing filters. These serve to protect the HEPA filters which follow. HEPA filters are the last stage of particulate collection.

Off-gas system design involves the following activities in terms of design criteria development:

- definition of melter feed composition and process rate
- determination of off-gas composition and rate
- determination of emission limits
- definition of safety and efficiency requirements.

In actual system design, the activities comprise selection of appropriate process equipment, specification of equipment, and design of controls and instrumentation.

The following sections address suggested approaches to each of these elements of the design process.

5.2 DEVELOPMENT OF DESIGN CRITERIA

Conceptual design of an off-gas system requires criteria that define feed conditions and performance requirements. Establishing conditions of the off-gas in turn requires an understanding of melter operation, and the ability to estimate how much of each component fed to the melter exits in the off gas. Similarly, system performance is fixed by a combination of emission regulations, operating safety, and design conservatism. This section addresses many of the requirements and considerations needed to establish the design criteria for an off-gas system.

5.2.1 Off-Gas Composition

Melter off-gas composition depends on feed composition, melter design, and melter operation. For a given melter and feed composition, the off-gas composition and flow rate are predominantly functions of the glass temperature, plenum temperature, cold cap size, inleakage, and slurry feed rate. These factors contribute to the variability seen in reported melter DFs. Design values for off-gas constituent concentrations must represent the upper limit of normal concentration variability, so that emission limitations are not exceeded. Prudent values can be chosen for design by comparing the predicted average and variability, and estimating the concentration which is two standard deviations above the mean. This gives a design value which would be exceeded only 5% of the time under normal operating conditions.

Melter performance is usually reported in terms of DFs, which are inversely related to concentrations. Design DFs for individual constituents can be calculated from melter performance data as follows:

$$DF \text{ (design)} = \frac{1}{\frac{1}{n} \sum_{i=1}^n \frac{1}{DF(i)} + 2 \sigma}$$

where DF(i) is the DF data point "i" for a specific component in the melter off gas, n is the number of data points, and σ is the standard deviation of all 1/DF(i) values.

Table 5.1 shows an example of reported melter DFs and Table 5.2 shows the corresponding calculation of melter design DFs for several constituents. The data was taken from a single melter run at PNL and does not represent recommendations for design values. Values for design purposes should be taken from data that closely relates to the design feed composition and melter conditions.

5.2.2 Off-Gas Emission Limitations

Removal requirements for airborne effluents are defined by regulations for both radioactive and hazardous compounds. Radionuclide release is limited by the maximum permissible concentrations as defined by 10 CFR 20 for facilities licensed by the Nuclear Regulatory Commission. Limits are placed on individual constituents and on the aggregate released. Further, 10 CFR 20 requires

TABLE 5.1. Example of Melter DF Data^(a)

Element	Melter DFs					Average DF
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	
Al	132	91	71	139	530	190
B	44	53	46	80	150	75
Cd	10	8.1	5.3	6.6	10	8
Cs	16	24	9	4.5	5.9	12
La	--	92	69	109	290	140
Sb	54	86	62	--	--	67
Sr	35	44	32	45	140	55
Te	6.3	3.3	4	6.1	8.5	5.6

-- = Data below detection limits.

(a) Goles and Sevigny 1983.

TABLE 5.2. Example Calculation of Design DFs

Element	Avg DF	K =		Std Dev of k, σ_k	K + 2 σ	Design DF = $\frac{1}{K - 2\sigma}$
		$\frac{1}{n} \sum_{i=1}^n$	$\frac{1}{nF_i}$			
Al	190	0.00835	0.00457	0.01749	57.2	
B	75	0.01650	0.00679	0.03008	33.2	
Cd	8	0.1327	0.0378	0.2083	4.8	
Cs	12	0.1214	0.07485	0.2711	3.7	
La	140	0.0095	0.0046	0.0187	53.5	
Sb	67	0.01543	0.00350	0.02243	44.6	
Sr	55	0.02238	0.00935	0.04107	24.3	
Te	5.6	0.1986	0.0757	0.350	2.8	

releases be controlled to a concentration which is "as low as reasonably achievable" (ALARA). The ALARA clause forces all reasonably practical and economical means be used in containing radionuclides below the listed maximum permissible concentration (MPC) values.

Emission limits for the off-gas discharge can be determined from the MPCs by applying an appropriate dilution factor between the stack and the site boundary. Dilution factors vary with topographical and meteorological conditions, and so are site specific. Dilution factors are determined from atmospheric dispersion data which is reported as χ/Q , where χ is the concentration at a point on the ground resulting from the discharge, and Q is the release rate at the stack. The dilution factor, D , can be calculated knowing the stack flow rate, F , from the equation:

$$D = \frac{1}{(\chi/Q) \times F}$$

Example dilution factors are shown in Table 5.3 for a few sites in the U.S. (Christian 1977). A design safety factor can be applied by allowing for less dilution than predicted by a meteorological model.

TABLE 5.3. Dispersion Data for U.S. Commercial Reprocessing Plants^(a)

Facility	$x/Q, \text{ sec m}^{-3}$	
	Maximum Offsite Annual Average, ^(b)	
	Ref. 83	Ref. 84 ^(c)
AGNS (Barnwell)	2.7×10^{-8}	2×10^{-7}
NFS (West Valley)	4.1×10^{-8}	3×10^{-6} inversion 2×10^{-6} average
GE (Midwest)	2.8×10^{-8}	4×10^{-8}

(a) Christian, J. D. and D. T. Pence 1977.

(b) Russell, J. L. and Galphin 1973.

(c) Kullen, B. J., L. E. Trevorow, and M. J. Steindler 1975

The MPCs tabulated in 10 CFR 20 represent values which may not be exceeded when averaged over one year when only that one radionuclide is present. For the normal case in which several radionuclides are present, the total discharge is limited such that the sum of the ratios of individual concentrations to the specific MPCs is not greater than unity. That is

$$\frac{C(a)}{MPC(a)} + \frac{C(b)}{MPC(b)} + \dots + \frac{C(n)}{MPC(n)} \leq 1$$

where $C(n)$ is the concentration in the n th radionuclide and $MPC(n)$ is the tabulated value in 10 CFR 20 for that radionuclide. Design values for stack concentrations should be established by first evaluating the decontamination predicted using ALARA-prescribed technology against the numerical concentration limits. This estimate can be made using DFs for process equipment meeting ALARA standards. Table 5.4 gives characteristic DFs for several devices commonly used in off-gas treatment systems. If the numerical concentration limit is not satisfied, then equipment must be added or revised and stack concentrations reevaluated. Once an adequate system is thereby developed, the predicted stack composition should be evaluated for sensitivity to excursions in individual radionuclides. The individual design concentrations should be

TABLE 5.4. Characteristic DFs for Melter Off-Gas Equipment^(a)

Equipment	Decontamination Factor	Effluent
Melter	1	Gas (iodine)
	4	Gas, semivolatile (ruthenium)
	40	Semivolatiles
	200	Aerosols
Ejector scrubber	2	Semivolatiles
	10	Aerosols and ruthenium
Hydro-Sonic® scrubber	1	Gas
	10	Aerosols
High-efficiency Mist eliminator	1	Gas
	10	Aerosols
Ruthenium adsorber	1	Aerosols
	1000	Gas (ruthenium)
Iodine adsorber	1	Aerosols
	500	Gas (iodine)
Tandem high-efficiency particulate air (HEPA) filters	1	Gas
	2000 ^(b)	Aerosols

(a) Based on data presented in Chapters 3 and 4.

(b) Estimated performance by Kessler and Randall (1984).

significantly lower than necessary to meet the aggregate limit, so that the annual average would not be exceeded if an excursion occurred for any one radionuclide. Prudent values can be chosen by relating DF variability with average DFs.

5.2.3 Normal Off-Gas Flowrate

The volumetric flowrate in the off-gas system governs the size of equipment and interconnecting piping. It is the sum of melter generated gases, inleakage of air to the melter, and cooling gas injected into the film cooler (or elsewhere in the system).

The contribution of the slurry feed to the off-gas can be estimated when the DFs can be predicted. Because melters can be operated under a wide variety of feed chemistry and temperature conditions, it is vital that the DFs used for calculation closely resemble predicted operating conditions. The factors which influence melter DFs are discussed in Chapter 3.0 of this report.

Melter inleakage is a function of the melter design, operating vacuum, and to a great extent, maintenance. Any uncontrolled leakage is undesirable, but it is not practical to develop an elaborate seal for melters operating in remote applications, so some leakage is accepted. A characteristic inleakage rate for PNL developmental melters operating at a negative pressure of 9 mm Hg is $0.75 \text{ m}^3/\text{min}$ per square meter of melter (glass pool) surface area. While this rate can rise dramatically with faulty connections, that condition is assumed not to exist in the design case.

Melter design feed rates are strongly dependent on the feed composition, and pilot tests are necessary to evaluate actual melting rates. A characteristic maximum slurry feed rate is between 75 to $100 \text{ l slurry/m}^2 \text{ h}$ of glass surface. Knowing the rates for inleakage and melter feed, the quantity of gas required for cooling in the film cooler can be determined.

Gas temperatures exiting the melter must be reduced below 400°C to minimize deposition of entrained particles on the pipe wall (Kessler and Randall 1984). Temperatures lower than 200°C are not desirable, as the risk of condensation increases and the presence of liquid on the pipe wall will promote rapid collection of solid material. Also, low temperatures may increase the rate of volatile salt deposition, notably alkali sulfates and borates. For a given melter design, the melter plenum gas temperature is dependent on the size of the cold cap and glass temperature. Melters with lid heaters generate plenum gas temperatures of $600\text{--}800^\circ\text{C}$ when operating. Melters with or without lid heaters generate temperatures approaching 1000°C when the cold cap is small or nonexistent, but this usually implies that the feed rate is correspondingly small. So taking the highest plenum temperature with the highest off-gas flow represents an extreme condition that is inherently conservative. The mass of cooling gas can then be calculated with a straightforward heat and mass balance

around the film cooler. The film cooler detailed design must accommodate the temperature range limitations mentioned above.

5.2.4 Maximum Off-Gas Surge Rate

The melter is normally controlled at a slight vacuum (about 9 mm Hg) to improve containment of radionuclides. Pressurization of the melter is undesirable for that reason, and also because an abrupt increase in melter pressure may force glass out of the melter discharge at an excessive rate unless the melter plenum and canister are coupled. Normal melter operation involves periods of surges that occur when a pool of aqueous slurry on the cold cap flows quickly onto the glass melt. Also, several abnormal mechanisms may lead to melter pressurization, including off-gas line or equipment blockage, excessive feed rate, loss of off-gas blowers, steam explosion, and combustible explosion. These must be addressed for system safety, but the surge event is a normal glass melting phenomenon and should be incorporated in the design criteria.

The frequency and magnitude of surge events has been correlated by SRL (Kessler and Randall 1984) from data collected during a 63-day run on their Large Slurry Fed Melter (LSFM). Using an exponential statistical model, they extrapolated the surge distribution data to allow prediction of the frequency of large surge events (Figure 5.2). As shown on the curve, surges greater than 7X were predicted to occur once every 200 days, while surges greater than 10X would be expected only once every 17 years. SRL chose to design the DWPF melter for a surge magnitude of seven times the normal off-gas flow rate.

Cold cap characteristics largely determine the amount of aqueous slurry that may pool on the surface, creating a surge potential. As such, surge distributions such as the one developed by SRL are specific to the feed composition, melter geometry, and feed rate employed, and should not be used for general design applications. However, the shape of the distribution would probably be similar for most melter conditions, and the methodology for developing the relationship is a valuable tool.

A design surge rate is defined as the maximum rate for which the off-gas system will maintain negative pressure during the event. The event must be

FIGURE 5.2. Off-Gas Surges in Savannah River Laboratory LSM

further defined as to the rate of increase and duration of the event. Figure 3.5 showed an example of a 3X surge event in which the off-gas flowrate peaked in 2 min. With this information, the pressure profile in the off-gas system can be modeled for the specific melter geometry and control system to determine the adequacy of the control system.

5.2.5 Design Values for Nonradioactive Gases

An off-gas composition that reflects the worst case conditions for each hazardous chemical compound must be established for normal operation.

Emergency conditions should be addressed with separate criteria. The design composition will be artificial, but appropriate for specification of off-gas treatment equipment. Safety factors should be included in the specification of equipment rather than in the design composition, so that equipment efficiencies and reliabilities can be individually considered.

5.2.5.1 Hydrogen

Melter feeds which include organics have potential for hydrogen evolution. There is no environmental emission limit for hydrogen, but it is highly flammable and must be controlled below flammability limits. The lower flammability limit (LFL) in air is 4% at room temperature and the lowest ignition temperature is 530°C. If oxidizing gases such as nitrous oxide are present the LFL may be even lower. Maximum flammable gas concentrations are normally limited to no more than 20% of the LFL. The choice of a design limit should allow for the maximum rate at which hydrogen concentration can increase, and the response time for corrective action.

5.2.5.2 Carbon Monoxide

The maximum permissible ambient concentration of carbon monoxide is limited by federal regulations to 10 mg/m³, but this limit is not stringent relative to the quantities likely to be emitted from a melter. Like hydrogen, carbon monoxide may be evolved from feeds which include organics, and concentrations must be maintained below the flammable limit, which is 12% in air.

5.2.5.3 Nitrogen Oxides

Nitrogen oxide emissions may be limited by either stack opacity or maximum permissible ambient concentrations. Stack opacity is inherently subjective, and may depend on environmental conditions as well as the gas concentration. As such, establishing a limit for emissions is imprecise. The maximum permissible ambient concentration is limited to an annual average value of 100 µg/m³. Essentially all nitrogen fed to the melter will appear in the off gas, so the maximum off-gas concentration can be derived from the maximum expected excursion in melter feed rate.

5.3 CONSIDERATIONS FOR EQUIPMENT SPECIFICATION

Several steps are involved in selecting and specifying off-gas process equipment. Once design criteria has been established, candidate devices may be screened for specific performance requirements. With a list of appropriate equipment in hand, the merits of each can be evaluated on the basis of relative performance, reliability, safety, remotability, space requirements, and cost. In many cases, the choice of one device influences the choice of others. Following equipment selection, specifications must be written for equipment capacity, efficiency, materials of construction, and other pertinent criteria. This section addresses considerations involved in selecting and specifying equipment.

Treatment equipment for off-gas emissions can be grouped into three functional categories: primary quench scrubbers, aerosol scrubbers, and gas scrubbers. Ancilliary equipment includes the film cooler, pumps, blowers, tanks, etc, which are discussed following the appropriate gas cleaning equipment. Depending on the equipment and gas composition, some treatment devices will perform two or three of these functions to some degree. Performance characteristics have been described for each of the candidate devices in previous sections. Other considerations are also important to equipment selection, including equipment reliability, form of collected material, utilities required, maintenance requirements, ease of operation, space requirements, and effects on related equipment or systems. These are discussed for each type of off-gas equipment included in this report.

5.3.1 Primary Quench Scrubbers

The first treatment step required for any melter system is cooling of the hot gases. The film cooler will introduce a significant cooling effect, but must operate well above the dew point to avoid condensation in the line. The primary scrubber is generally used to provide additional cooling, condense steam, and remove the larger particulate material. Because water is used as the collecting medium in these devices, they also provide some degree of gas scrubbing capability. Cooling of the gas is a desirable first step because

downstream process equipment must operate at lower temperatures for process efficiency and because construction materials specifications can be less stringent.

5.3.1.1 Ejector-Venturi Scrubber

The ejector-venturi scrubber has been used industrially for many years and has a proven record of reliable operation. Because there are no internal moving parts, little opportunity exists for equipment malfunction. The particle collection and cooling effects result from the direct contact by high speed water droplets, which capture particles and provide high surface area for efficient transfer of heat by vaporization. High scrubbing solution velocities have their penalties, however. Melter gases often include highly corrosive components, which may be adequately contained by various alloys. For alloys that depend on the deposition of an impervious oxide layer for corrosion resistance, the high velocities and erosive action in the ejector-venturi throat may make them unacceptable due to erosion of the protective layer.

The weak link in ejector-venturi reliability is the high pressure (~30 to 50 psig) pump for scrub solution recirculation. Any rotating equipment in a remote handling area introduces the opportunity for failure and resulting maintenance requirements. The combination of the fine solids, corrosive liquid, and high pressure make sealing the pump shaft a critical maintenance item. This is further complicated by limitations on elastomers that will withstand the radioactive environment.

A recirculation tank and associated level controls make up the remaining elements of the ejector-venturi scrubber system. The tank should be agitated or constantly circulated to maintain collected solids in suspension. Because the scrub solution picks up large quantities of heat (about two-thirds of the heat generated by melter electrodes) from the gas, this tank must be provided with some means of cooling.

Ejector-venturi scrubber operation is normally quite stable and easily controlled. Direct control of performance is possible by adjusting the solution recirculation rate. The ejector-venturi will induce a draft in the off gas, relieving some of the duty from the off-gas blower.

The space required for the ejector-venturi is relatively small. A unit designed to handle an off-gas volume of 200 cfm would occupy a space approximately 1 ft by 1 ft by 4 ft high. This is an advantage in designing the equipment arrangement and in reducing the conduit length from the melter. Of course, the total space requirements must include the recirculation pump and tank.

5.3.1.2 Submerged Bed Scrubber

The SBS is a passive device and requires no external pump or tank. Liquid circulation is induced by the bouyant effect of the rising gas, and is relatively slow. As such, there is no erosive action and construction material selection need only address the corrosive effects of the solution. However, because cooling is supplied to the scrub solution by internal helical coils, the low circulation rate requires a large heat transfer surface area. The low rates may also foster tube fouling in some applications and this can become a significant factor in long-term operation.

Material captured in the scrubbing solution generates a sludge that must be purged. One approach is to enclose the entire SBS within another tank, allowing the SBS to overflow (Figure 5.3). The outer tank is equipped with cooling coils, and the collected solids can be agitated and transferred back to the melter feed makeup tank by using an eductor or pump.

Depending on the proportion of air and steam in the off gas and the bed operating temperature, the scrubbing solution may either condense steam from the off gas or be stripped by it. This lends some flexibility to operation, but requires level control for both conditions. When condensing, the SBS could be allowed to simply overflow, but when being stripped, makeup solution must be supplied. If the bed is operated at the saturation temperature, of course, no change in level occurs. This last mode of operation could be implemented by controlling the bed temperature to maintain level. The optimum operating temperature may be a compromise between potentially improved scrubbing efficiency at lower temperatures (because of steam collapse) and increased concentration of collected material when being stripped. In this latter operating mode, the SBS serves as an evaporator, to some extent.

FIGURE 5.3. Submerged Bed Scrubber Within Overflow Tank

With no internal moving parts, the SBS maintenance requirements are minimal and onstream reliability should be very high. Fouling of the bed or tubes may develop in long term operation, but experience at PNL has demonstrated that most solid depositions are not tenaciously attached. The gas entrance to the SBS is submerged in the scrubbing solution, resulting in an area near the pipe exit that undergoes rapid changes in temperature. The resulting condensation of steam encourages deposition of solids in that short pipe section. This

tendency was essentially eliminated at PNL by diluting the off gas with air in the film cooler, and maintaining high gas velocities in the line. The completely passive operation of the SBS obviates the weaknesses of rotating equipment such as wear, shaft sealing, and the need for lubrication.

Several features influence SBS performance, including bed cross sectional area, type of packing, packing height, gas distributor design, tank dimensions, and cooling coil design. Most of these features require compromises in various measures of performance, and pertinent considerations are addressed in the following discussion.

The packed bed cross section determines the superficial gas velocity in the bed, which in turn affects the scrub solution circulation rate. Absorption and condensation efficiency are influenced by the liquid to gas ratio (L/G), and this ratio peaks at a minimum stable value. Figure 5.4 shows the relationship between L/G and superficial gas flow rate as determined by Hilliard et al. (1981) for an SBS. This curve is specific to the type of packing and gas distributor used and will not be accurate for SBS design using other internals, but it does illustrate the operating characteristics for this equipment.

FIGURE 5.4. Liquid-to-Gas Flowrate in Submerged Gravel Scrubber as Reported by Hilliard et al. (1981)

Design details can be determined from the appropriate L/G versus gas flow-rate relationship. This curve is an important indicator of performance, because scrubbing efficiency of both gases and particulates should be improved with higher L/G values; however, an accurate correlation between L/G and particulate scrubbing efficiency has not yet been developed. Using the curve in Figure 5.4 as an example, the L/G reaches a maximum at a gas velocity less than 0.1 m/s, and precipitously drops off as gas velocity decreases. This rapid drop in L/G is the result of unstable, surging flow conditions occurring at low flowrates, which should be avoided in design and operation. At gas flowrates higher than this point, the L/G declines and circulation rates will also decline, so there is an incentive to design for low velocities. A compromise is required between performance and physical equipment size (and cost) to provide the necessary safety margin for operation above the unstable region. Judgment must be used to select the design L/G, as it directly affects the bed cross-sectional area (equipment size), and the fluid circulation rate (scrubbing performance).

Because flow of the off-gas and scrubbing solution are concurrent, gas scrubbing performance can be estimated for a given SBS with known dimensions by assuming the bed to be a single stage contactor. In experimental applications the SBS has not been used for gas absorption, but gases soluble in the scrubbing solution are absorbed unless the solution concentration approaches equilibrium with the off gas. If only partial removal of a particular gas is required (as may be the case of NO_x), the SBS may offer sufficient removal capability by replenishing the solution at a rate that controls the concentration at a low level.

Packing shape influences mass and heat transfer rates, which tend to improve with increased surface area. However, complicated packing shapes also collect more solids, making high-efficiency packings impractical. The packing used in PNLs pilot scale SBS is 3/8-in.-diameter ceramic marbles. The spherical shape offers the lowest surface area per unit volume, but remains clean in operation. The PNL SBS has accumulated 760 hours of operation during various experiments without significant solids deposition.

Hydraulic behavior is determined by the length of upper and lower skirts, bed depth, and bed submergence. The upper skirt is needed to contain the bed packing, and the lower skirt contains the inlet gas below the packed bed. As the bed depth increases, the absorption efficiency increases, but so does the gas side pressure drop. Hence the design value requires a compromise between scrubbing efficiency and energy loss. PNL's experimental SBS includes 61 cm of packing depth, a 7-cm upper skirt, and a 25-cm lower skirt. Performance of this configuration has been tested under off-gas flowrates ranging up to 150 scfm, and particulate DFs have been relatively consistent. However, the efficiency in cooling the gas stream has not been as consistent, as off-gas temperatures have at times been 20 to 30°C hotter than the solution temperature. The 61-cm depth should probably be considered a minimum for particulate scrubbing until equipment performance can be estimated more accurately, and the depth required to achieve a given degree of gas absorption or gas cooling may be greater. The SBS designed by PNL for West Valley included a bed depth of 96.5 cm, and 25-cm-high gas injection risers to assure good gas distribution. Normal design practices are adequate for selection and sizing the gas distributor, but the annular shape of the packed bed makes the use of commercially available equipment difficult.

The high off-gas pressure drop requires that all equipment following the SBS be operated at a relatively high vacuum. The SBS designed for West Valley will introduce a 122-cm (water column) pressure drop to the gas stream. With the melter operating at a nominal vacuum of 13-cm (water column), the equipment following the SBS must operate at 135-cm. A vacuum this high requires exceptionally good sealing features to prevent inleakage, and presents a significant challenge for remote equipment operation and maintenance.

Cooling Coils

The cooling coils must be designed to remove heat from the scrubbing solution at the highest rate likely to occur, which requires knowledge or estimates of the heat transfer coefficient and the temperature of cooling water available. Heat transfer load on the coils is a combination of the sensible and latent heats of the off-gas, reaction heat (if reactions occur), and the heat of solution of dissolving gases. Of these, the heats of reaction and solution

are usually negligible. The greatest heat load will occur when the film cooler is operating with steam injection, and the off-gas is being evolved from the melter at the highest design rate. If the film cooler will operate with air only, the highest rate will occur when the air injection rate is low. It is not necessary to accommodate the design surge on an instantaneous basis, as the volume of solution is large and the temperature will change little with a brief change in off-gas rate.

The heat transfer coefficient can be estimated from handbooks using cross-flow correlations. This estimate will be appropriate for clean conditions, and must be reduced to account for fouling. PNL's experience has shown that the overall heat transfer coefficient with clean coils may be in excess of $150 \text{ Btu/ft}^2 \text{ hr F}$. The fouling that will occur will reduce that figure, and PNL used $100 \text{ Btu/ft}^2 \text{ hr F}$ as the design overall coefficient for the West Valley SBS.

Cooling coils may fail in service, requiring replacement. This would be very difficult or even impractical in a remote application, and zoned coils are recommended so that the leaking section can be isolated from service. Three zones, each with 50% of the required heat transfer area, will allow one zone to fail without reducing process rates. If two zones failed the process rate would be limited, but some additional cooling could be introduced by increasing the flow of injection air.

5.3.2 High Efficiency (Aerosol) Scrubbers

5.3.2.1 Hydro-Sonic® Scrubber

The Hydro-sonic® scrubber requires a motive jet of air or steam to atomize the scrubbing solution through the use of a sonic nozzle. The small nozzle orifices are susceptible to blockage by solids, requiring filtration of the scrubbing solution. The HSS system is analogous to the ejector-venturi, but uses less water. Its recirculation fluid is also cleaner than that of the ejector-venturi. Onstream reliability should be quite high, but will depend on the cumulative failure rates for the pump, filter, and nozzles. The motive air or steam should be quite clean so as not to introduce additional aerosols which could interfere with downstream filters. The space required for a Hydro-Sonic®

scrubber itself is reasonably small. A 200-cfm unit would occupy a space of approximately 1 ft x 5 ft x 5 ft. A tank and circulation pump will require additional space.

Introducing motive air or steam into the off-gas stream will influence downstream equipment design criteria. If air is used it will increase the volume of gas that must be treated, possibly requiring larger equipment. If steam is used and later condensed, the volume of liquid waste byproduct increases. Steam may provide better scrubbing than air would because of condensation, but this effect has not been quantified.

The volumetric operating range is quite good for this device, as flowrates of motive gas and scrubbing solution can be independently adjusted to maintain optimum performance. Collection efficiency for a given off-gas rate and aerosol distribution depends on both rates, and will tend to improve with increased solution injection rates (Wright 1982). There will be a maximum liquid rate corresponding to flooding, that is manifested as instability in the discharge pressure. Normally, the motive gas will cause a rise in off-gas line pressure across the device.

As discussed in Chapter 4, the collection efficiency is apparently not influenced by treatment with another identical scrubber. Savannah River Laboratory has investigated the performance of two steam-driven Hydro-Sonic® scrubbers in series, and report similar DFs for each one. The series arrangement has been incorporated in the DWPF design.

5.3.2.2 High Efficiency Mist Eliminator

A HEME can be used following the initial quenching step which creates a cool and humidified gas. The capture mechanism in an HEME can be both inertial and by diffusion (Brownian movement), but since initial off-gas scrubbing removes larger particles (greater than 10 microns), the HEME should be designed for particles exhibiting significant Brownian motion. Small particles are captured by diffusing to the liquid film on the fiber, where they become included in the liquid phase. Liquid and soluble solid particles will become part of the film, whereas insoluble solid aerosols may lodge on the fiber and become physically bonded. The HEME can also be operated dry (above the dewpoint), and

in this mode it is essentially a deep-bed washable filter. Dry operation minimizes the migration of compounds soluble in water, and thereby decreases penetration and reentrainment. Backflushing with a spray of water or cleaning solution will dislodge a majority of collected particles, but the insoluble material will accumulate, requiring eventual cartridge replacement.

Because collection of aerosols depends on diffusion effects, performance is improved with increased residence time in the fiber bed. It follows that the turndown ratio is unlimited, as collection efficiency will increase at lower flows. Flow through the element is normally from outside to inside to take advantage of the larger outside surface area for collection. This is particularly important for gas streams containing solid aerosols.

The HEME has been used industrially for collection of acid mists and aerosols since 1964 and has well documented performance characteristics. There are no internal moving parts, and onstream reliability is very high. The most likely failure would be blinding of the fiber bed by material from failed upstream scrubbing equipment. Routine maintenance will involve changing the fiber element cartridge when the pressure drop following backflushing remains high. This procedure requires the element be dry to minimize contamination, and a source of dry air or heat is necessary (Furrer 1980).

The backwashing spray used to clean the element of collected material may be used continuously or intermittently. When used continuously, the pressure drop through the packed fibers will be markedly higher because of the reduction in flow area available for the gas stream. Flushing generates additional liquid which must be recycled for treatment, and must be minimized. The optimum flushing program is a compromise between the gas pressure drop across the element and the quantity of liquid generated. Frequent flushing with small amounts will maintain a fairly steady pressure drop, but consumes more liquid. Infrequent flushing with a large quantity reduces the net amount of liquid needed, but the pressure drop will rise until flushing is completed. Furrer conducted tests on a HEME to determine the effect of backflushing frequency and volume on the pressure drop and particle retention in the bed. These tests were conducted on HEME elements that had been loaded with a radioactive salt. In the first case, a single large flush restored the element to clean

condition; in the second case six small flushes were used. The results of those tests are shown in Figures 5.5 and 5.6, which demonstrate the compromise between pressure drop and flushing quantity. In the single flush case the total liquid volume was 75 L, compared to 105 L applied in six small flushing steps to achieve the same degree of cleaning. Periodic flushing, however, introduces a lower peak pressure drop during the cleaning cycle.

HEME elements are commercially available in many materials and configurations, and manufacturers will assume responsibility for some specifications, such as packing density, fiber diameter, and packed depth.

The inlet gas flowrate will largely determine element size, and should be taken as the discharge rate from the primary scrubber corresponding to the

FIGURE 5.5. HEME Backwash in Small Flushes

FIGURE 5.6. HEME Backwash with Single Large Flush

melter discharge design rate. Performance is not strongly affected by temperature changes of the magnitude likely to occur, and the design temperature can be the steady state value. The inlet particle size distribution and loading are key criteria, and values should be chosen which correspond to design surge conditions in the melter.

Polypropylene may degrade in the radioactive environment, but is highly resistant to chemical environments. Glass fiber packing has a higher aerosol collection efficiency, is very resistant to radioactivity and acids, but severely degrades in the presence of alkaline solutions.

5.3.2.3 Ruthenium Guard

Ruthenium can be evolved from the melter as a gas. Because it can be a major contributor to radioactive emissions, a sorbent bed may be desirable to ensure even small amounts do not escape. Several sorbents have been tested under various conditions, but performance data varies widely, and cannot be used without careful examination. Other methods and materials have been investigated for ruthenium capture, but the results are incomplete for design purposes. Further design-oriented work is needed for this unit operation.

5.3.2.4 Iodine Guard

The most effective method for removal of iodine from the gas stream is in a sorbent bed. Various silver impregnated substrates are available that will yield very high efficiencies; however, some are adversely affected by NO_2 in the gas stream.

The most effective solid sorbent materials for iodine capture appear to be silver zeolite (AgX) and silver mordenite (AgZ). Because of the low acid resistance of AgX, AgZ is probably more appropriate for LFCM application, and some design-related information will be given here for this type of bed. This material is 18 wt% silver and is prepared for the synthetic sodium mordenite Zeolon.[®] The effectiveness of AgZ is increased by hydrogen pretreatment, which causes reduction of silver to its elemental form (Burger and Scheele 1983); this material is designated Ag[°]Z.

Reasonable design parameters, based on results of testing with a bed of Ag[°]Z (as reported by Holladay 1979) are given as follows:

- superficial face velocity, 15 m/min
- operating temperature, 150°C
- loading capacity, 120 mg I_2 /g Ag°Z.

I_2 was fed to a 5 cm diameter by 15 cm long bed at a concentration of 1500 mg I_2 /m³. The DF at breakthrough was 10³ to 10⁴. Both the loading capacity and the DF could be substantially lower if such a sorber is used in LFCM service because iodine concentrations are likely to be much lower and because of the potential for interfering halogen gases. The loading capacity above assumes no other halogens present. The design capacity should be calculated based on the total concentration of halogens; if radioactive iodine is 1/10 of total halogens (mole basis), then the effective iodine capacity is 12 mg I_2 /g Ag°Z.

Because most iodine from reprocessing is volatilized during dissolver operations, the quantities reaching the melter are likely to be low, as will the resultant LFCM off-gas concentrations. The DF obtained in the above test was for iodine concentrations corresponding to dissolver off-gas conditions. The effectiveness of silver mordenite at very low iodine concentrations (but still high enough to be of concern with respect to current emission regulations) has not been established.

Sorbent beds are generally highly reliable, very flexible to changes in operating rates, and require little space. Because the sorbent must be replaced once loaded, a redundant system is necessary to provide continuous onstream capability. Holladay (1979) describes methods for regeneration, but these may not be practical for remote LFCM applications. High loadings are desirable to minimize sorbent consumption. Loadings can be increased by installing two beds, the first of which would be operated until nearly fully loaded, and the second to maintain the necessary DF. After the first bed is loaded, it is recharged with sorbent from the second bed, and the second bed is recharged with fresh sorbent. In this manner, all sorbent is nearly fully loaded and the highest possible DF is achieved. The percentage of sorbent loading can be calculated by monitoring the composition of the inlet gas. Operating experience will be necessary to establish practical operating limits for sorbent loading.

5.3.2.5 Film Cooler

A drawing of the film cooler used in PNL's PSCM is shown in Figure 5.7. This device introduces a boundary layer of steam or air on the pipe wall at the entrance to the off-gas line. As shown, the cooling gas enters an annular space which is partitioned by a corrugated curtain. The gas flows down the outer side of the curtain to the bottom of the film cooler, and turns 180 degrees to flow upward and through several circumferential slots. The injected gas lowers the temperature of the pipe wall and the off gas, thereby reducing the tendency for particles of entrained glass or feed material to stick to the pipe wall.

The primary concern in designing a film cooler is providing sufficient cooling to reduce solids accumulation in the jumper. However, other operational parameters are also influenced by the film cooler, including superficial gas velocity, melter pressure, and combustible concentration. Using the limiting criteria for each of these, the maximum flow of cooling gas can be established, and the number of slots and the slot width can be determined. The slots must be designed such that the flow of cooling gas remains laminar as it is introduced into the off-gas jumper. The slot angle, length, width, and exit shape all are important to this criteria.

The film cooler used at SRL on their TNX melter includes a brush reamer which can be used periodically to remove material which collects on the inner wall. They report that the cooling effect provided by the film cooler results in a friable, easily removed accumulation (Kessler and Randall 1984).

5.4 INSTRUMENTATION AND CONTROLS

This section addresses feedback control loops, data acquisition recommendations, alarms, primary and final control elements, and special considerations for remote applications.

5.4.1 Process Control

A simplified off-gas system schematic is depicted in Figure 5.8. The two greatest difficulties in operating pilot-scale melters have historically been keeping the off-gas line clean and maintaining the melter vacuum within

FIGURE 5.7. Film Cooler Used in PNL PSCM

FIGURE 5.8. Schematic of Off-Gas System Controls

specified limits. Introducing a film cooler into the system has ameliorated both of these problems, and has introduced new control requirements. Melter pressure must be maintained within a narrow range for safe and efficient melter operation. Pressure can be controlled by modulating the flow of cooling gas (air or steam) being injected into the film cooler or off-gas line. However, tests conducted at PNL have shown that the velocity in the off-gas line should be maintained above 15 m/s to minimize solids deposition, and the off-gas temperature may have maximum and minimum limits. Further, additional air may be required to dilute combustible gas below an explosive concentration. For normal operating conditions, the setpoint on the flow controller for the film cooler is set at a constant design value.

Melter pressure is controlled by adjusting the volume of dilution gas being injected downstream of the film cooler. Upstream of control valve CV-2, this gas should be maintained at a constant pressure to improve control. The

setpoint for this controller is established by the operator to be consistent with melter design. Because the melter is subject to surge in normal operation, the response of this loop must be quite rapid.

Jumper gas temperature is controlled by adjusting the total flow through the off-gas system with CV-3. The temperature controller is cascaded to a flow controller operating on the off-gas exit. In this manner, the flow range can be restricted so that a minimum flow will always be present, and thereby maintain the minimum off-gas jumper velocity. Under surge conditions, the flow of dilution gas would be throttled back to maintain melter vacuum, causing the jumper gas temperature to rise rapidly, which would in turn require an increase in the exiting off-gas flow.

Modeling of this proposed system would be essential to determine the appropriate controller time constants. If controllers are not properly tuned, instabilities could occur which may lead to melter overpressurization.

5.4.2 Data Acquisition

Process data must be collected for process control and for later analysis. Because the process is necessarily remote, more data points and redundancy are appropriate than in conventional processes. Surge events offer the best opportunities to evaluate system behavior, so all flow rates, pressures, and temperatures should be recorded frequently enough to clearly indicate the system response. Ordinarily this will mean either continuous (analog) records, or digital records taken every few seconds. Longer term phenomena, such as filter pressure drop history, can be effectively illustrated with data points taken every 15 minutes.

Digital records of operation are desirable because they permit easy manipulation and direct computer analysis. However, real time operations require the operator to frequently check the value and trend of certain variables. Analog records such as conventional strip charts are desirable for the melter pressure, cooling gas injection rate, combustible gas concentration, and key temperatures.

5.4.3 Alarms

Process alarms are necessary to alert the operator of abnormal conditions that may lead to unsafe conditions for personnel or equipment. The off-gas system is the last line of defense in capturing radionuclides emitted from the melter. Because the off-gas system has a very short residence time for the gas being treated, alarm points on control logic that may lead to emergency venting must be set at conservative values. This will allow sufficient time for the operator or automatic emergency measures to correct the problem or shut down the process before an accidental release of radionuclides could occur.

Melter pressure is the most important process variable to control within the design range, and excessive pressure must engage an emergency relief system. If the emergency system is unable to completely treat the surge volume of off gas, a serious excursion in radionuclide emissions may occur. As discussed in Section 5.2.4, surge events are not explosive, but ramp up steadily over a period of time that is determined in part by the melter plenum volume. This finite time period allows for orderly and effective responses if the alarm condition is initiated at an early point. A possible approach would be to use both the differential and the absolute value of the pressure function to signal an alarm. This could potentially allow setting a warning alarm point at a lower value, by requiring both the rate of rise and the absolute value be above a given level to before an emergency response would occur.

Many other alarm points will be required in any off-gas system, which can be alarmed in a conventional manner.

5.4.4 Primary and Final Control Elements

Automatic process control is necessary to operate the off-gas system in a remote, radiation environment. To facilitate maintenance, only the primary (sensing) and final (controlling) elements are placed in the remote location; all intermediate signal modifiers and controllers can be located outside the remote process environment. This section describes applications for some of the control elements for flow, liquid level, temperature, and pressure.

5.4.4.1 Flow Measuring Elements

Conventional primary elements satisfactory for sensing flow include head-type meters (orifice, ejector-venturi, pilot), electronic rotameters, magnetic flowmeters, and displacement meters. Each has advantages and limitations in off-gas systems.

Head meters sense the difference in pressure between specific locations, so compressible fluids such as steam or air should be maintained at a stable pressure upstream of the element. The velocity profile affects the pressures being sensed, and must be uniform at the approach to the element. This means that the effective size of a head meter must include the length of the straight run of pipe or straightening vanes necessary to assure a uniform profile.

The orifice system has a useful minimum to maximum flow range of about 3 to 1. The measurement of flow ratio beyond the range of a particular installation can be accomplished by either changing the size of the orifice or allowing a greater pressure drop across the orifice. It is recommended primarily for clean fluids such as air, steam, or water where it is accessible for maintenance. Permanent head loss across an orifice depends on design and flow rates and may be 50% of the measured differential. It is therefore not recommended for use in recirculating lines where it would increase the head required on a pump, as increased head is often accompanied by increased maintenance. The high head loss also makes it less desirable for measurement of the off-gas flow.

The venturi meter provides the ultimate in pressure recovery, and will permit accurate measurement of approximately two-thirds more fluid than an orifice at the same differential head. Also, the streamlined entrance and exit make deposition of solids less likely to occur than in an orifice. The chief disadvantages are the larger relative size, and lack of flexibility. The orifice is relatively easy to replace if the flowrate range must be changed, whereas the venturi throat is fixed and the entire unit must be replaced. The venturi meter is well-applied in the off-gas line following the treatment equipment, but is too large to be considered for most other applications.

The pitot tube offers the lowest resistance to flow, but sacrifices accuracy to do so. It has a tendency to plug more easily than other elements, has a more limited velocity range, and is sensitive to abnormal velocity distribution effects. Therefore, it has little application for off-gas systems.

The magnetic flowmeter measures volumetric flow rate and is not affected by density, viscosity, and fluid pressure. It requires a conductive fluid, hence it is not used for gas service. Since the device measures flow, a uniform velocity profile is not necessary; however, the meter does not have to be completely filled with fluid for an accurate measurement. This element offers no obstruction to the flow path and is the best choice for slurries or streams that tend to plug, such as primary scrubber solutions. It is available in a variety of materials, and can be used on highly radioactive streams. The flow range for a specific element is about 25 to 1, and they are available from 0.13 l/min and up.

Rotameters are usually designed for a flow range of 10 to 1, but larger ranges are available. Electronic rotameters operate on the same principle as conventional rotameters, but have electronic transmitters incorporated into the design. Because measurement depends on the movement of a float within a tube, this device is poorly suited to fluids containing entrained solids. Rotameters are generally not recommended for flows below 0.4 l/min. For smaller flows, the magnetic flowmeter should be considered.

Inexpensive displacement meters can be used to measure the volume of water transferred where rate measurement or control are not necessary.

5.4.4.2 Liquid Level Detection

Recirculating solutions for primary and secondary scrubbing and gas absorption will require surge tanks with level detection. The simplest device commonly used is the conventional purged dip tube. It works well in applications where liquids have a uniform specific gravity, and can be adapted to give a specific gravity reading as well. It is not well applied in solutions which are close to saturation with salts, as the air purge has a tendency to cause

localized precipitation which will eventually plug the tube. Since it is simple and relatively easy to maintain, it is recommended wherever plugging is not expected.

Conductivity probes and capacitance probes have been used in remote applications and are available in radiation resistant materials. These devices can be used for either continuous level measurement or alarm points.

5.4.4.3 Temperature Measurement Devices

Devices acceptable for temperature measurement or switching include resistance thermometers, filled-system thermometers and switches, and thermocouples.

The resistance thermometer exploits the inherent change in metal electrical resistance with temperature. It is available in materials that will withstand temperatures up to 540°C and high gamma radiation exposures. Tests have been conducted at Hanford to determine the service life of resistance thermometers in a high radiation environment. Temperature elements, as received from several manufacturers, were subjected to an accumulated gamma radiation exposure of 8×10^9 Roentgens (R). The results indicated that elements properly sealed would last indefinitely. Other elements failed after a gamma exposure of 1×10^9 R due to radiolytic decomposition of water vapor which leaked into the element (Waste Management Technical Manual).

Thermocouples have been used extensively in the radiation environment and are recommended where temperatures exceed the range of resistance-type elements.

Filled system thermometers are recommended for temperature measurement where a record is not required. Some filled-system thermometers are also equipped with snap-action switches to provide high/low limit trip points for alarms.

5.4.4.4 Pressure Measurement Devices

Most conventional pressure gauges and transducers will operate in the radiation environment if elastomers are not used for diaphragms or casings.

Transducers can be located outside of the radiation environment by using purged sensing lines if the purge air does not adversely affect the process.

5.4.4.5 Control Valves

Diaphragm air-operated control valves are available in designs especially for use in the radioactive environment. These valves have body designs that allow complete drainage when the plug is off the seat ring and the valve is installed in a jumper to allow the liquid to return by gravity to a vessel. Special construction and double seals protect the pneumatic line from intrusion by radioactive solutions. Diaphragms of Buna N rubber with nylon inserts can withstand a total gamma exposure of 1×10^9 R before failure. The life of the diaphragm can be improved by placing a lead shield around the chamber. Neoprene diaphragms with nylon inserts can withstand 1×10^8 R.

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