Mercury Recovery from Phosphor Powder

NORTH AMERICA
TECHNICAL SOLUTIONS

www.VeoliaES.com

VEOLIA
ENVIRONMENTAL
SERVICES

History

- **Tallahassee Facility**
  - **January 2001, facility found to be out of compliance with 99% recovery rate**
  - **Sampling plan and permit required monthly calculation of recovery rate**

History

- **Decreasing mercury concentration in lamps**

T-12 Lamps	
Year	Mercury mg/lamp
pre-1992	41
1992-1996	30
Current	<9.5

T-8 Lamps	
Year	Mercury mg/lamp
pre-1992	30
1992-1996	15
Current	<5

Variance

VEOLIA ENVIRONMENTAL SERVICES

- **Initial Variance issued January 2002**
  - Contained alternate schedule for demonstrating compliance
    - Pre-retort >1000 mg/kg must achieve 99%
    - Pre-retort <1000 mg/kg must reach <10 mg/kg final
  - Required testing of process alternatives
    - Increased process times
    - Inserting metal rods to serve as heat conductors
    - Inserting a perforated pipe in center of drum to facilitate removal of mercury vapors
  - Initially approved for 2 years and extended 1 additional year
  - Results of process alternative testing did not significantly improve recovery rates

Permit Renewal

- **Sampling Plan revised**
  - Demonstrate on a semi-annual basis as opposed to monthly
  - Calculate to nearest whole percent
  - Began using new sampling plan second half 2005
  - Successfully met requirements of new plan until first half 2009

First Half 2009

- **Facility achieved a recovery rate of 98% (98.3)**
- **Veolia notified FL DEP Regional Office of results**

	Sample ID	Mercury Total Before Processing	Mercury Total after Processing	Percent Recovery
JAN	NSA0118	448		
	NSA0121		4.04	
FEB	NSB0134	771		
	NSB1124		9	
MAR	NSC1344	502		
	NSC1231		3.95	
APR	NSD0484	512		
	NSD2026		16.5	
MAY	NSE0579	334		
	NSE2500		5.75	
JUN	NSG0319	306		
	NSG0420		8.55	98%

What Happened

- **As of April 2009**
  - **Recovery rate still at 99%**
  - **Based on Recovery Rate as of April powder released for off-site shipment**

	Sample ID	Mercury Total Before Processing	Mercury Total after Processing	Percent Recovery
JAN	NSA0118	448		
	NSA0121		4.04	
FEB	NSB0134	771		
	NSB1124		9	
MAR	NSC1344	502		
	NSC1231		3.95	
APR	NSD0484	512		
	NSD2026		16.5	
				99%

What Happened

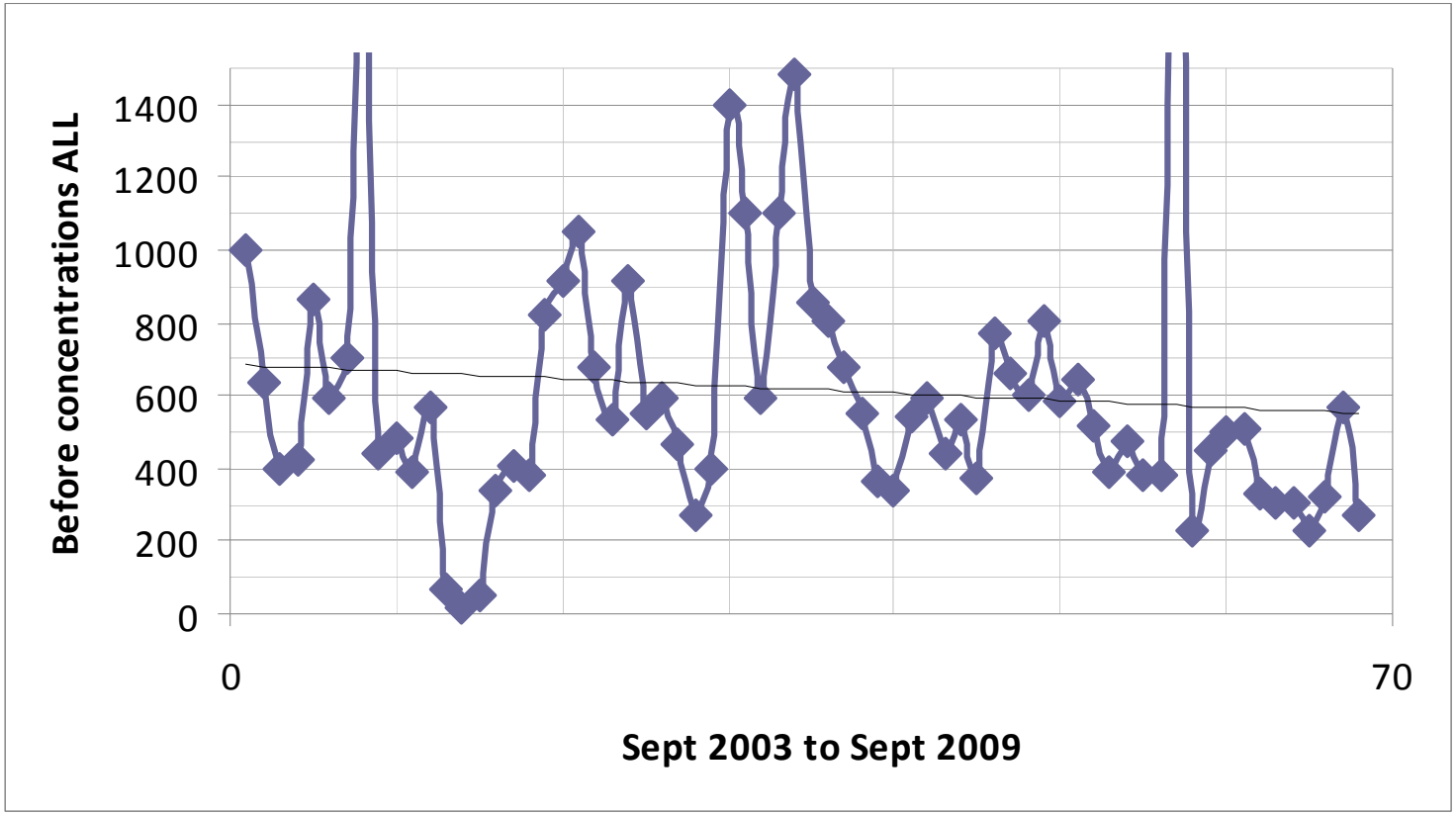
- May and June pre-retort analysis both reported back <350 mg/kg
- June material reprocessed in an attempt to achieve lower post retort results
- Material reprocessed, reported at 13.3 mg/kg

	Sample ID	Mercury Total Before Processing	Mercury Total after Processing	Percent Recovery
JAN	NSA0118	448		
	NSA0121		4.04	
FEB	NSB0134	771		
	NSB1124		9	
MAR	NSC1344	502		
	NSC1231		3.95	
APR	NSD0484	512		
	NSD2026		16.5	
MAY	NSE0579	334		
	NSE2500		5.75	
JUN	NSG0319	306		
	NSG0420		8.55	98%

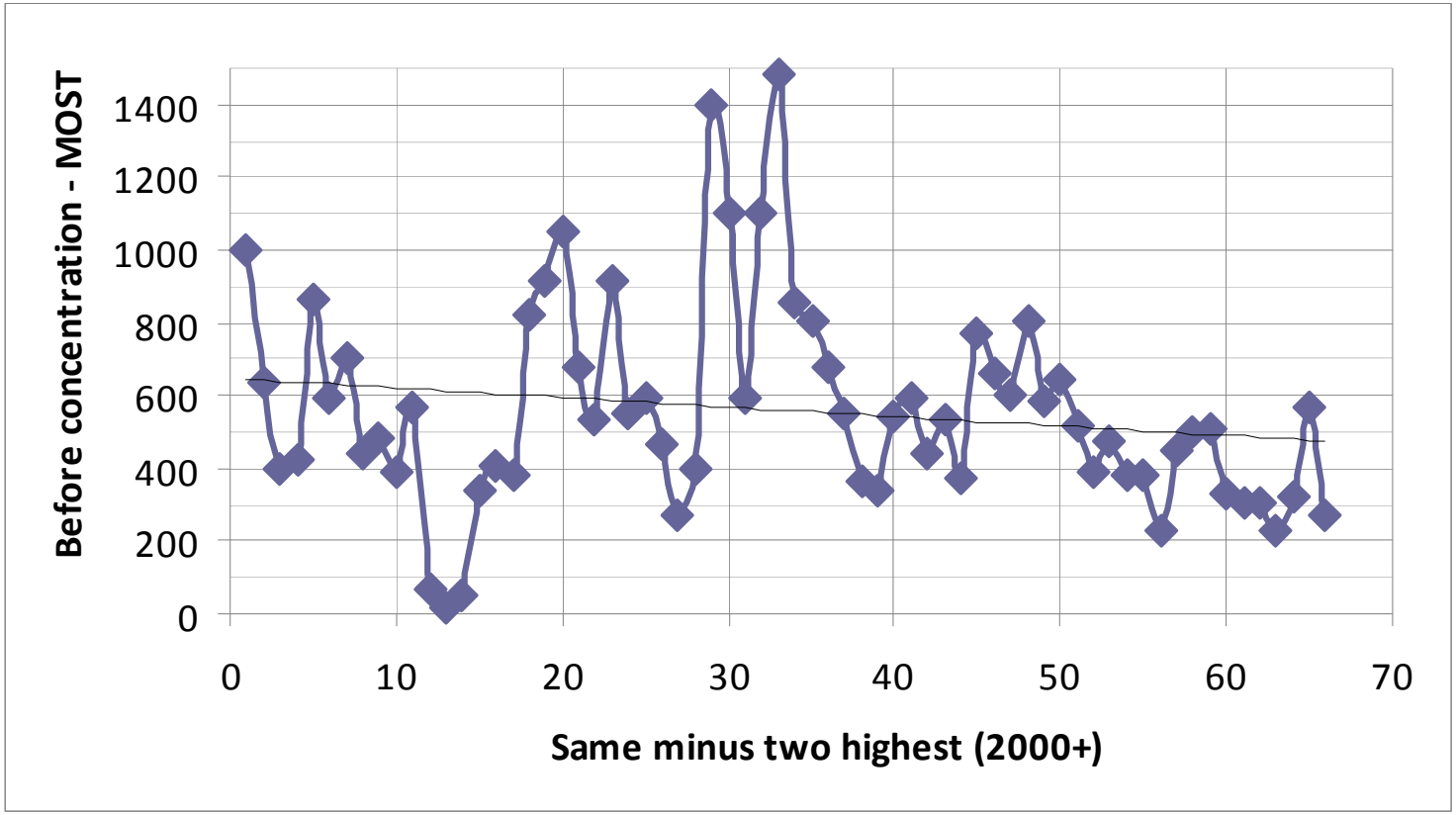
Analysis of Problem

- **Original Hypothesis**
  - Lower concentration of mercury in lamps is lowering the concentration of mercury in the phosphor powder.
- **Review of Data**
  - Results of pre and post retort analysis supplied to FL DEP
  - Several graphs put together by Jim Byer

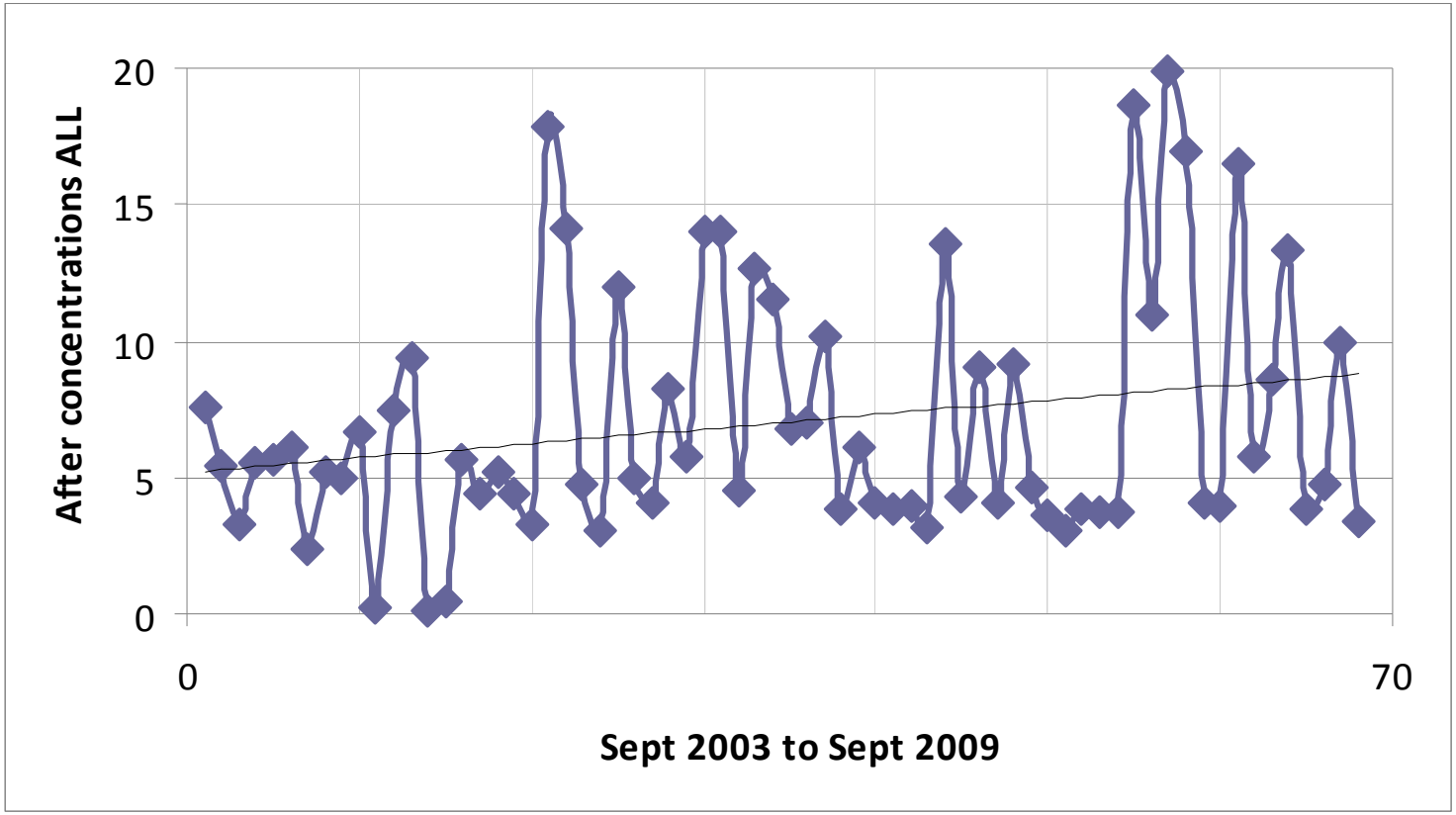
Pre-retort Results



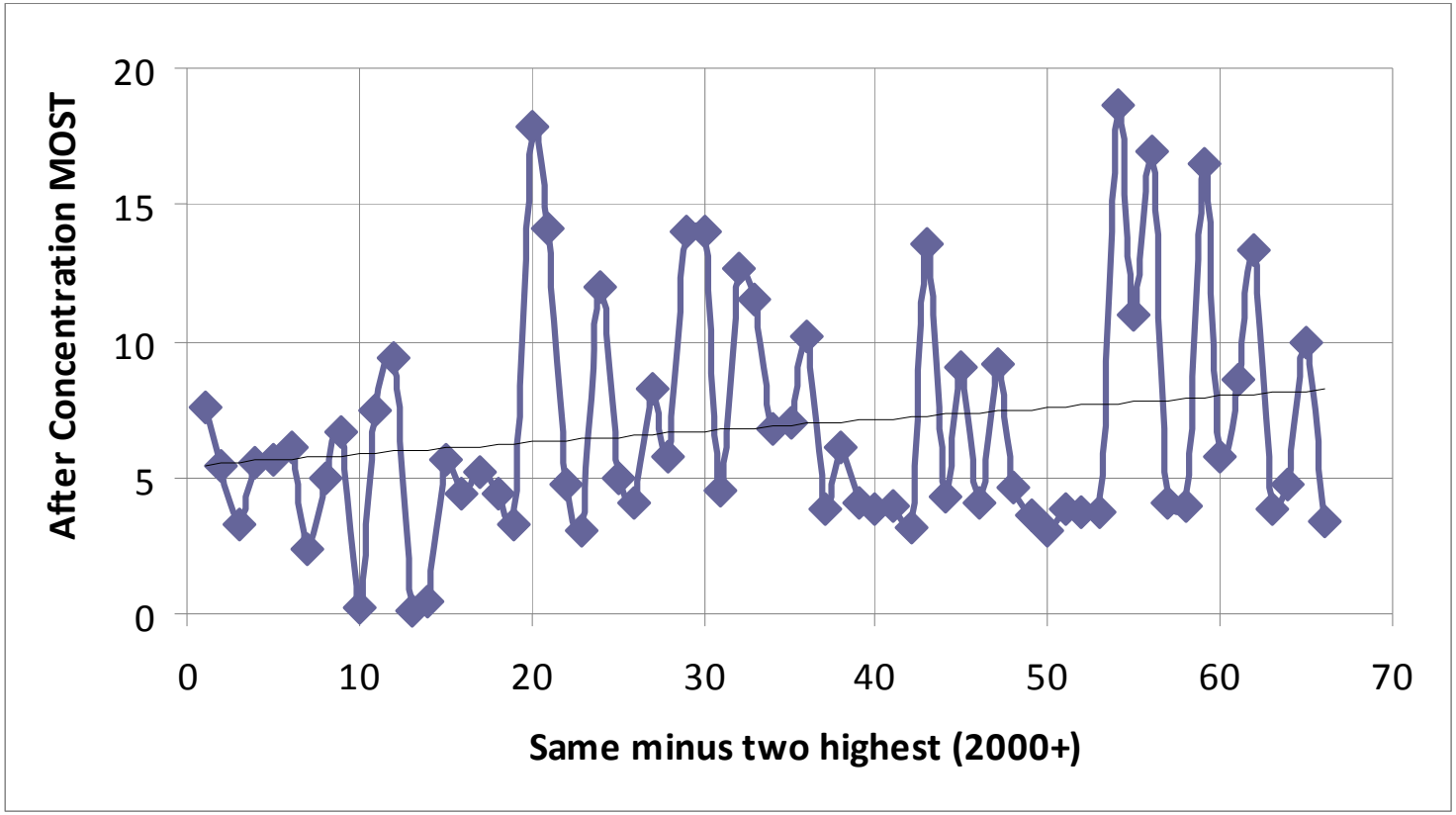
Pre-retort Results



Post-retort Results



Post-retort Results



Analysis of Data

- **Original hypothesis only partially supported by data.**
  - **Pre-retort analysis continues to trend downward**
  - **Post-retort analysis is trending slightly upward**
- **Why would post-retort results trend upward**
  - **No changes to the retort equipment being used**
  - **No change to the temperature set points of the oven**
  - **No changes to the vacuum system**

Factors reviewed

- Effect of reprocessing
- Powder composition
- Results compared to recovery rates for other materials
- Results compared with other Veolia facilities
- Results compared with non-Veolia facility

Effect of Reprocessing

VEOLIA ENVIRONMENTAL SERVICES

- During the months of November and December 2008 and June 2009 all powder retorted was processed a second time in an attempt to lower the concentration of mercury

	Post-retort	Post-retort reprocessed
November 08	18.6 mg/kg	11 mg/kg
December 08	19.9 mg/kg	16.9 mg/kg
June 09	8.5 mg/kg	13.3 mg/kg

Powder Composition

VEOLIA ENVIRONMENTAL SERVICES

Location		Tallahassee	Port Washington	Stoughton	Phoenix	Port Washington
Powder Chemical analysis (FX)	CaO	22.57	28.06	23.62	15.73	27.62
	MnO2	0.62	0.67	0.6	0.29	0.68
	Sb2O3	***0.29***	***0.33***	***0.34***	***0.17***	***0.36***
	SrO		1.6	0.81	0.54	0.73
	BaO	0				
	MgO	1.15	1.56	1.5	1.89	1.23
	Al2O3	4.5	2.68	1.93	4.33	3.71
	SiO2	30.98	31.87	38	47.56	29.99
	K2O	0.49	0.34	0.31	0.4	0.31
	Fe2O3	0.23	0.32	0.39	0.27	0.47
	Na2O	5.37	5.56	7.15	9.03	5.45
	P2O5	16.6	17.91	16.35	8.58	19.31
	La2O3	2.05	1.02	1.16	1.34	1.39
	CeO2	1.97	0.9	1.15	1.1	1.21
	Tb4O7	0.69	0.35	0.38	0.43	0.45
	Y2O3	10.4	4.98	4.87	6.3	5.81
	Eu2O3	0.65	0.32	0.33	0.38	0.37
	Gd2O3					

Powder Composition

VEOLIA ENVIRONMENTAL SERVICES

Concentration in mg/kg		
Antimony	2540	1930
Arsenic	45.7	56.9
Beryllium	ND	ND
Cadmium	26.8	28.2
Chromium	8.03	6.05
Copper	1470	1260
Lead	436	95.2
Magnesium	619	485
Manganese	4170	3160
Nickel	83.9	61.3
Selenium	ND	ND
Silver	14	28.2
Thallium	ND	ND
Zinc	238	265

Powder Composition

- New energy efficient lamps use Tri-ban phosphor (triphosphor) as opposed to halo phosphor
  - Tri-ban phosphor
    - Barium magnesium carbonate or aluminate
    - Rare earth elements
  - Halo phosphor
    - Calcium halophosphate
    - Antimony
    - Manganese
- Could presence of rare earth elements or other metals be adversely impacting the recovery rates

Powder Composition

- Contacted an engineer from Veolia's Port Arthur incinerator who is degreed in metallurgy
  - No simple way to calculate the strength of an amalgam formed and no reference material readily available
- Contacted a major manufacturer of fluorescent lamps
  - Submitted recovery data and composition data from R&D project conducted by Veolia Environnement
  - Based on a review of the data and their own internal testing in developing phosphors, chemical composition of the phosphor should not significantly alter recovery rates
  - Presence of copper or zinc which are not typically used in phosphors but was found in the powder may be derived from material used to cement end caps to tubes
  - Lamp manufacturing techniques have changed and the materials used to coat the phosphor on the lamps has changed

Lamp Manufacturing process

VEOLIA ENVIRONMENTAL SERVICES

- Early tri-ban lamps were originally coated with a layer of halo phosphor before being coated with tri-ban phosphor
- Now tri-ban lamps are coated with activated alumina before being coated with tri-ban phosphor
- Activated alumina is a porous material with an extremely high surface area to mass ratio

Material	Surface Area
Halo phosphor	6 m^2/g
Tri-ban phosphor	3 m^2/g
Activated Alumina	30 m^2/g

Comparison with other materials

VEOLIA ENVIRONMENTAL SERVICES

- Compared recovery rates for powder versus crushed arc tubes from HID lamps
- Both processed using same program for time, temperature and vacuum
- Arc tubes comprised primarily of quartz glass and bits of material with a relatively course particle size

Average Recovery Rate Data 2007 - 2009			
	Before	After	Percent Recovery
Phosphor Powder	606.86	7.58	98.8%
Arc Tubes	1193.82	1.13	99.9%

Comparison with other materials

- Veolia Port Washington processes several mercury amalgam waste streams
- Zinc amalgam from battery manufacturer
  - Processing time 48 hours
  - Processing temperature 1100° F
  - Final concentration after one time in process >3000 mg/kg
  - Final concentration after second time in process 750 mg/kg
- Silver amalgam from dental waste
  - Processing time and temperature the same as zinc
  - Final concentration after one time in process average <5 mg/kg

Comparison with other Veolia locations

- **Veolia Stoughton MA facility**
  - Use MRT brand retort units
  - Use smaller cans for powder, stacked 4 high in retort

	Average post-retort powder	Average post-retort arc tubes	Surface area open to oven
Stoughton	6.48	0.90	2.18 in^2/lb
Tallahassee	7.58	1.13	0.82 in^2/lb

Comparison with other facilities

- Contacted competitor to discuss recovery rates
- Competitor did not provide specific data but acknowledged that our results from Tallahassee were slightly lower than results they obtain
- This particular facility operates a continuous feed retort process
- The process uses an auger to move the powder through the heating chamber which causes the powder to be agitated as it is heated

Conclusions

- Presence of zinc in powder may be impacting final concentration
- Presence of activated alumina is most likely cause of upward trend in post-retort powder
- 99% can be achieve right now but if post-retort concentrations continue to trend upward or there is any deviation in results the required recovery cannot be achieved

Recommendations

VEOLIA ENVIRONMENTAL SERVICES

- **Revise the rule requiring 99% recovery rate for phosphor powder**
  - One alternative is to lower the rate in the rule
  - Second alternative is to change the rule to make the recovery rate a part of a facility's sampling plan and include it as a permit condition.
- **Second alternative would be preferred alternative**
  - Allows department flexibility to establish recovery rates based on material being processed
  - Allows department flexibility to adapt to changing material composition
  - Would still allow for public involvement in the process