Life Cycle Impact Analysis of Cd in CdTe PV Modules

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NATIONAL PV EHS ASSISTANCE CENTER

- Investigate potential environmental, health and safety (EHS) hazards for new photovoltaic materials, processes and applications
- 180 Publications/Web Site (www.pv.bnl.gov)

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CdTe PV Life-Cycle Stages (focus on Cd Flows –Air Emissions)

1. Mining/Smelting/Refining
2. Purification of Cd & Production of CdTe
3. Manufacture of CdTe PV modules
4. Utilization of CdTe PV modules
5. Disposal of spent CdTe PV modules

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Perceptions

"**GreenPeace is deeply concerned** with the possibility of the CPA choosing to purchase solar modules that contain toxic metals…Current **CdTe panels** result in **Cd (gaseous) emissions of 0.5 g/GWh, equivalent to that of a coal fired power plant. The majority of these emissions (77%) result from <u>mining</u> and <u>utilization</u> of the modules** … "

Comment to the California Power Authority, 2002

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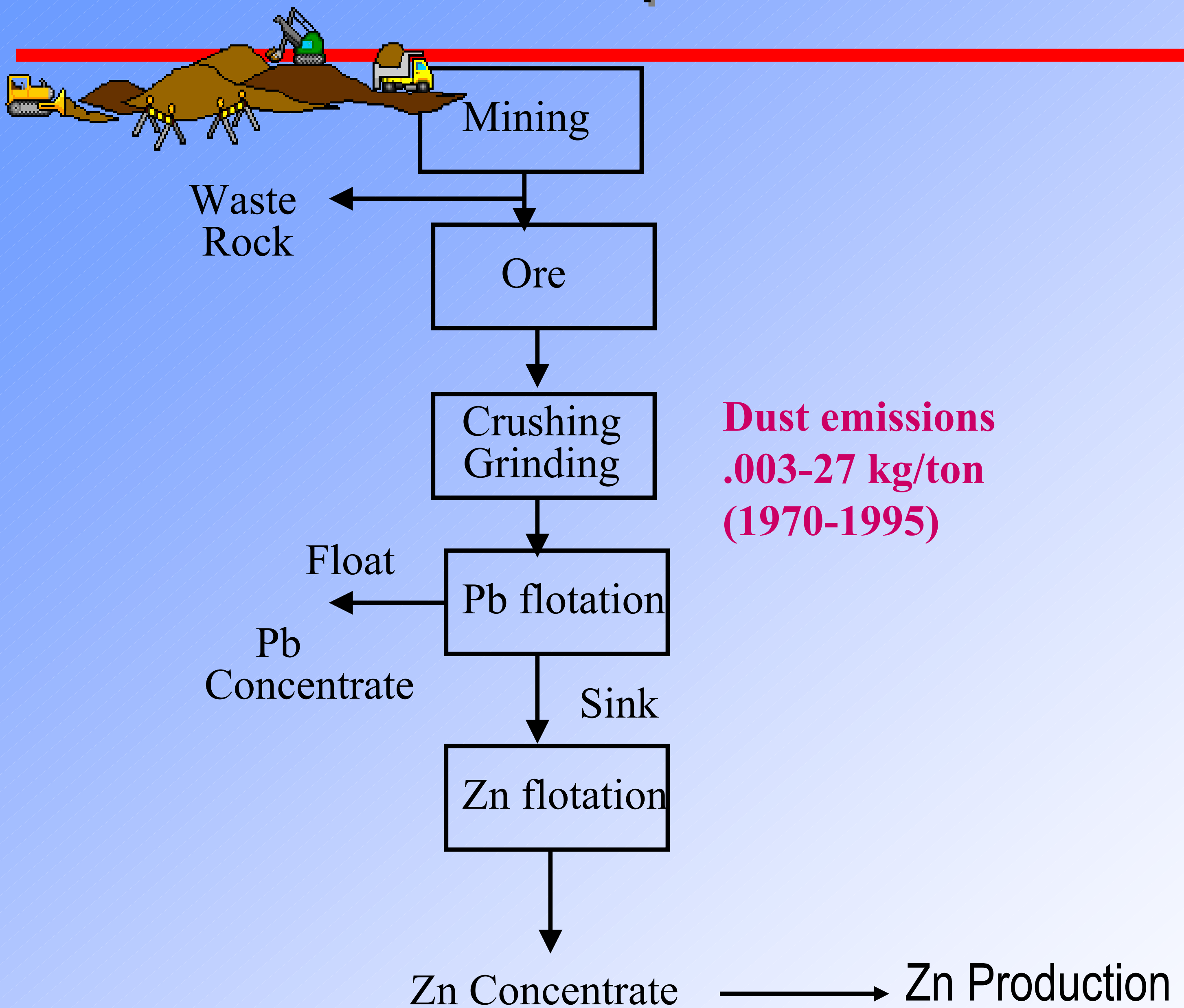
Cd Flows in Zn Mining
-Atmospheric Emissions-



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Emissions Coefficients for Production of Toxic Heavy Metals

- Emission coefficients and estimates abound and differ

  (CGA 1973, 1981; Davis 1972; NAS 1980; PEDCo, 1980; NRC 1977, 1981; Nriagu 1980a, 1980b, 1980c; Niagu and Davidson, 1982; USEPA 1984; USEPA, AP-42, 1995; Liewellyn, US Bureau of Mines, 1994; Berdowski et al., Insp. Env., Netherlands;1995 ; Pacyna, EC, 1990)

- Best Approach -Combination of material balance and plant-specific emissions data
- Sources used:
  - US: Survey of (Cd Emission Sources (GCA, 1981; US Bureau of Mines, 1994; Plashy, USGS, 2001)
  - EC: Berdowski et al., 1995, 2003; Pacyna, 1990
  - UK: National Atmospheric Emissions Inventory, 2002
  - TeckCominco Trail plant, Canada, 1999-2003
  - Asarco Glove plant, Denver, 2000-2003

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EC Emission Factors for Primary Zinc Production (g/ton product)

	Germany 1991		Poland 1980-1992		Holland 1992	Europe 2002	
Compound	Thermal	Electrolytic	Thermal	Electrolytic	Electrolytic	Thermal	Electrolytic
Cadmium	100	**2**	13	**0.4-29**	**0.5**	50[1]	**0.2**
Lead	450	1	31-1000[2]	2.3-467	-	1900	-
Zinc	-	-	420-3800	47-1320	120	16000	6

1 with Imperial smelting furnace.
2 limited abatement.

Sources: Berdowski et al., 1995, 2003; Pacyna, 1990

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Production and Emissions at the Trail Smelter and Refineries, British Columbia, Canada [Teck Cominco Ltd, 2003]

Annual Production (ton)	**1998**	**1999**	**2000**	**2001**	**2002**
Zinc	274,300	288,700	272,900	168,100	269,000
Lead	63,900	75,700	91,300	55,200	80,700
Cadmium		1,400	1,400	1,400	1,400
Specialty Metals		28	28	28	28
Silver	463	431	463	348	670
Gold	3	2	2	2	5
Fertilizer	273,000	240,700	220,300	167,500	225,000
Cd Releases to Air from all Operations (kg/yr)		600	250	100	95
(g of Cd/ton metal products)		**1.64**	**0.69**	**0.45**	**0.27**
Cd Releases to Water from all Operations					
(kg/yr)		208	290	170	208
(g of Cd/ton metal products)		0.57	0.79	0.76	0.59

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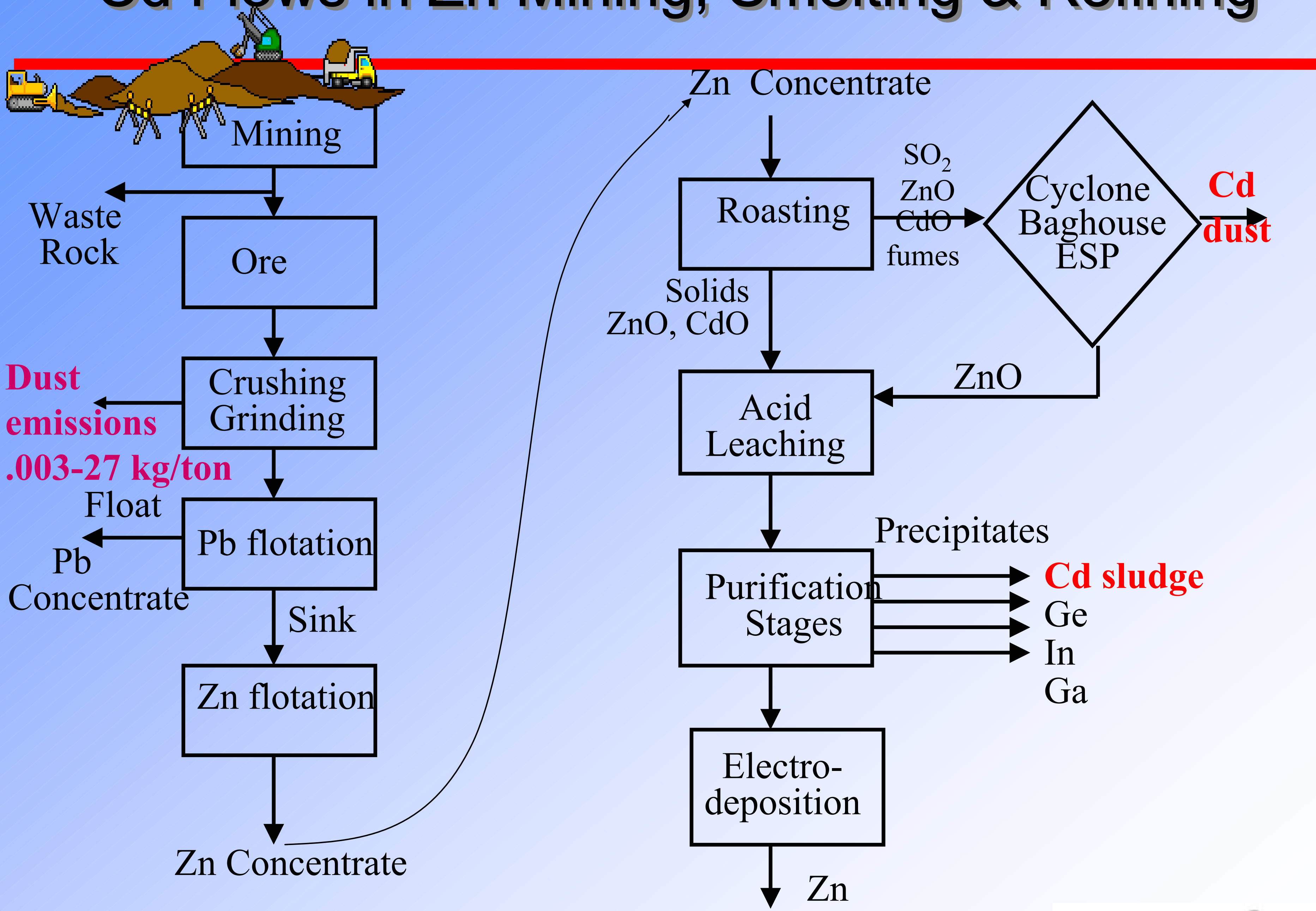
Cd Flows in Zn Mining, Smelting & Refining



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Cd Emissions from Mining/Smelting: Facts

1. Cd is a byproduct of Zn, Cu and Pb production. The main resource of Cd is CdS in sphalerite (ZnS) ores. The Zn/Cd ratio is 200/1 to 350/1.
2. Production of Cd uses emissions and waste of Zn production
3. Cd output is dependent on Zn production, not on Cd demand
4. Before Cd production started in the US, ~85% of Cd from Zn concentrates was lost to the environment
5. Zinc mines in the US also produce:
   - 100 % of Cd, Ge, In, Th
   - 10 % of Ga
   - 3 % of Au,
   - 4 % of Ag

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Emissions Allocation based on Material Output from Zn-ore

Metal	Typical Grade in ore (ppm)	Emissions Allocation (%)
Zn	40000	99.44
Cd	200	0.50
Ge	20	0.05
In	4	0.01

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Emissions Allocation based on the Economic Value of Products from Zn-ore

Metal	Typical Grade ore (ppm)	Prices 1998* ($/kg)	Primary Production (10^3 ton/yr)	Production Economic Value (10^6 $/yr)	Emissions Allocation (%)
Zn	40000	1.1	7000	7700	97.82
Cd	200	0.6	20	46	0.58
Ge	20	1700	0.05	70	0.89
In	4	306	0.2	56	0.71
Total				7872	100

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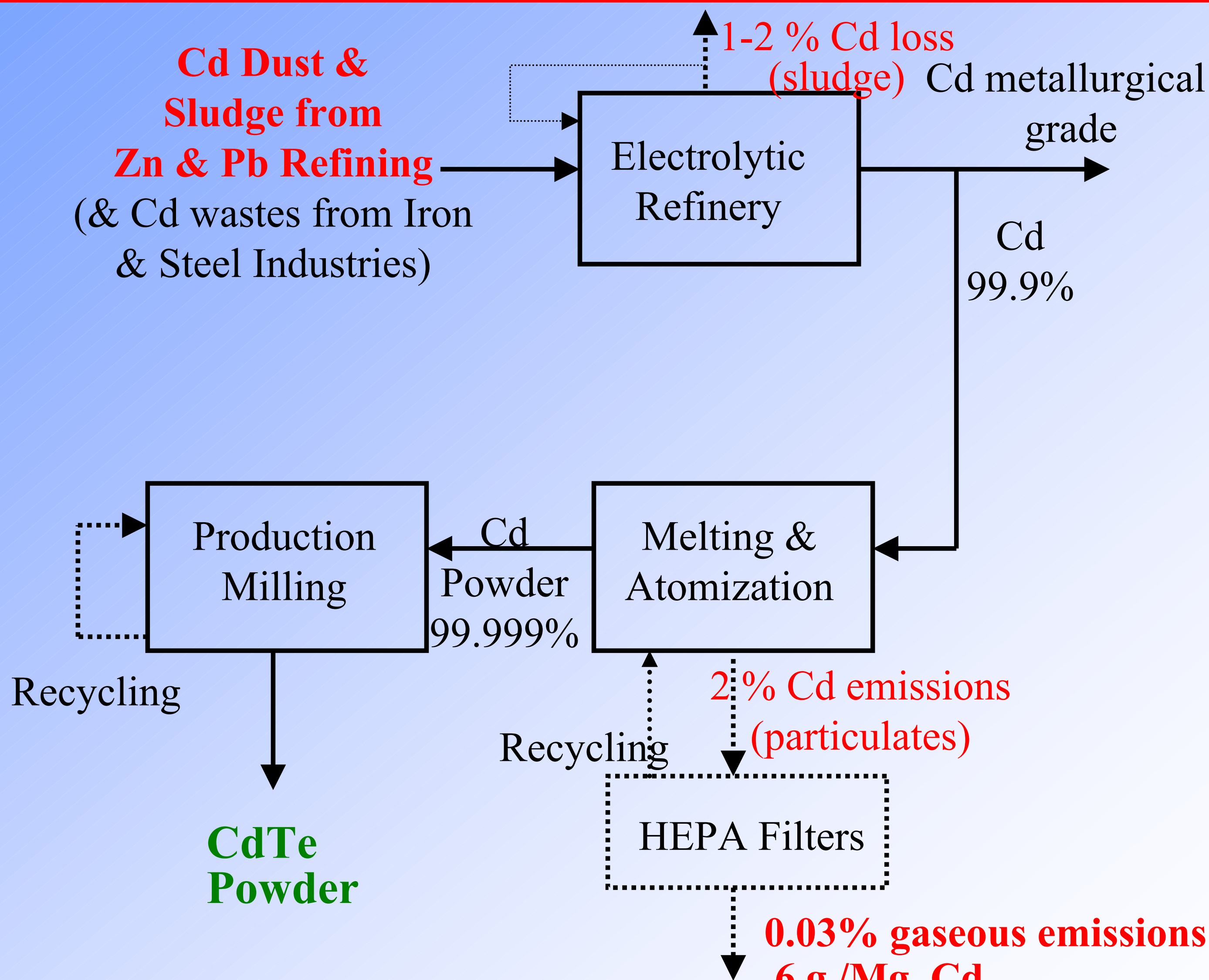
Cd Flows from Cd Concentrates to CdTe



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Cd Emissions in CdTe PV Manufacturing

- **High-Rate Vapor Transport Deposition**

35-70% material utilization
Residuals are recycled
1% of vapors carried in exhaust
99.97% collection via HEPA filters

Controlled Cd emissions=3 g/Mg Cd input

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Utilization of CdTe PV Modules

- **Zero emissions under normal conditions**

  (testing in thermal cycles of –80 C to +80 C)
- **No leaching during rain from broken or degraded modules** (Steinberger, 1997)
- **Debate on fire risks**
  - Thermogravimetric tests on CdTe powder and single-glass CdTe PV (Steinberger, 1998)
  - Glass-CdTe-Glass PV

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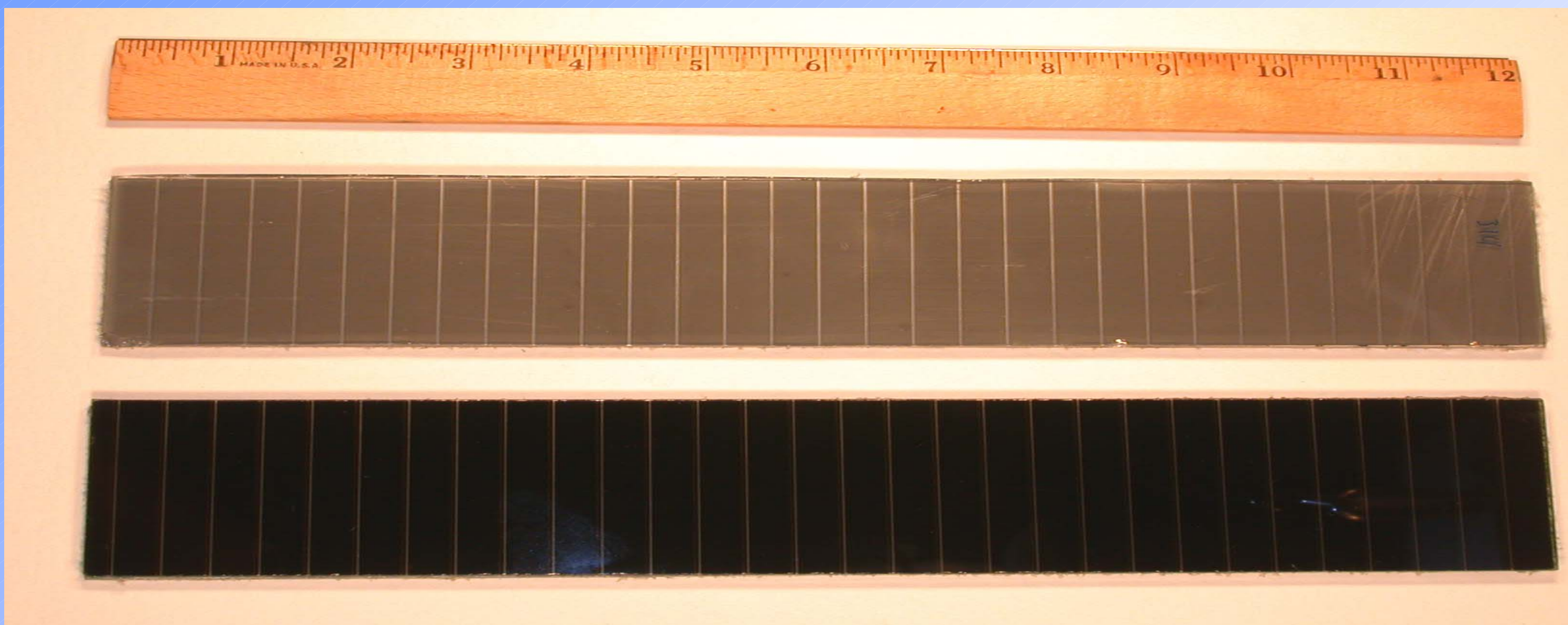
CdTe PV sample for fire-simulation experiments



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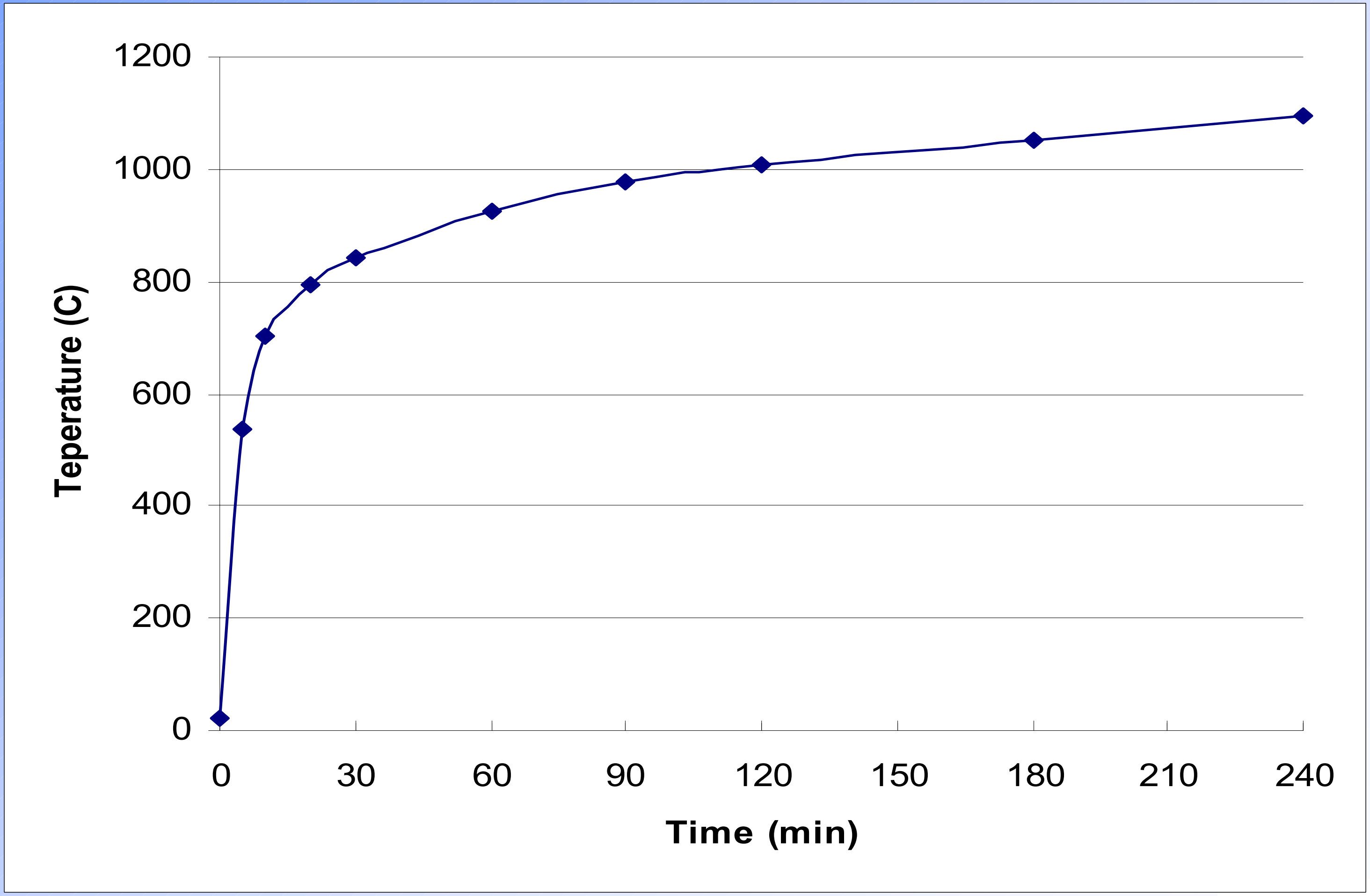
Fire Simulation -Test Protocols

- UL 1256 30 min @760 C
- ASTM E119-98 Standard Temperature Curve



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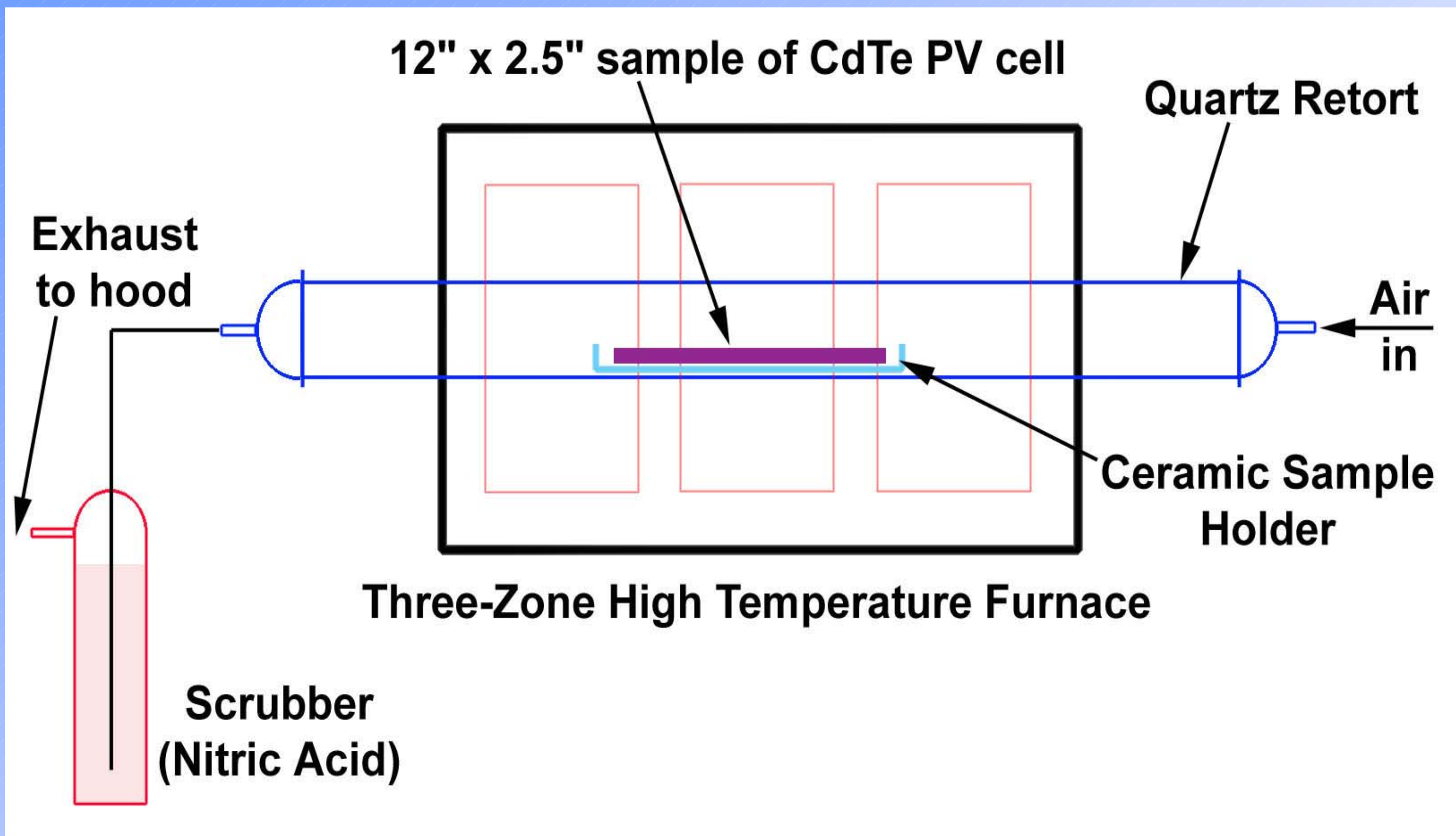
Fire Simulations Experimental Set-up



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Fire-simulation Experiments

- Weight Loss Measurements
- ICP Analysis of Cd & Te Emissions
- X-ray Fluorescence Micro-Spectrometry of Cd in Heated Glass
- ICP Analysis of Cd & Te in Heated Glass

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Thermogravimetric & Emissions Analysis

Temp (C)	Weight Loss (% sample)	**Cd Loss (% Cd)**	Te Loss (% Te)
760	1.9	**0.6**	0.4
900	2.1	**0.4**	1.2
1000	1.9	**0.5**	11.6
1100	2.2	**0.4**	22.5

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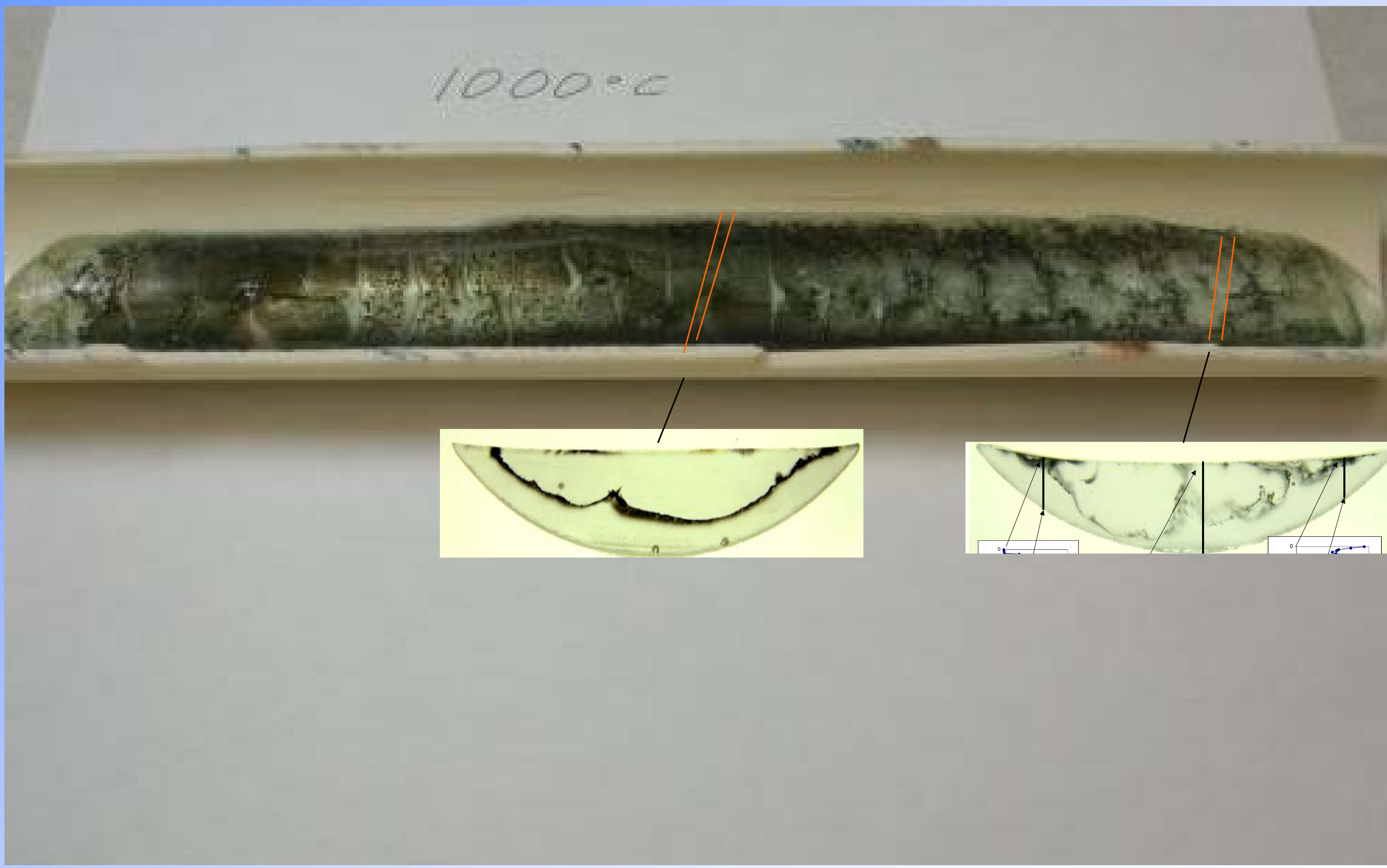
Heated Sample –1000 C



Heated Sample –1100 C

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National Synchrotron Light Source

Provides small, intense beams of X-rays for many analytical techniques:

Microbeam x-ray fluorescence (XRF)
ppm to ppb sensitivity for many elements

X-ray absorption spectroscopy (XAS)
metal redox state, atomic coordination

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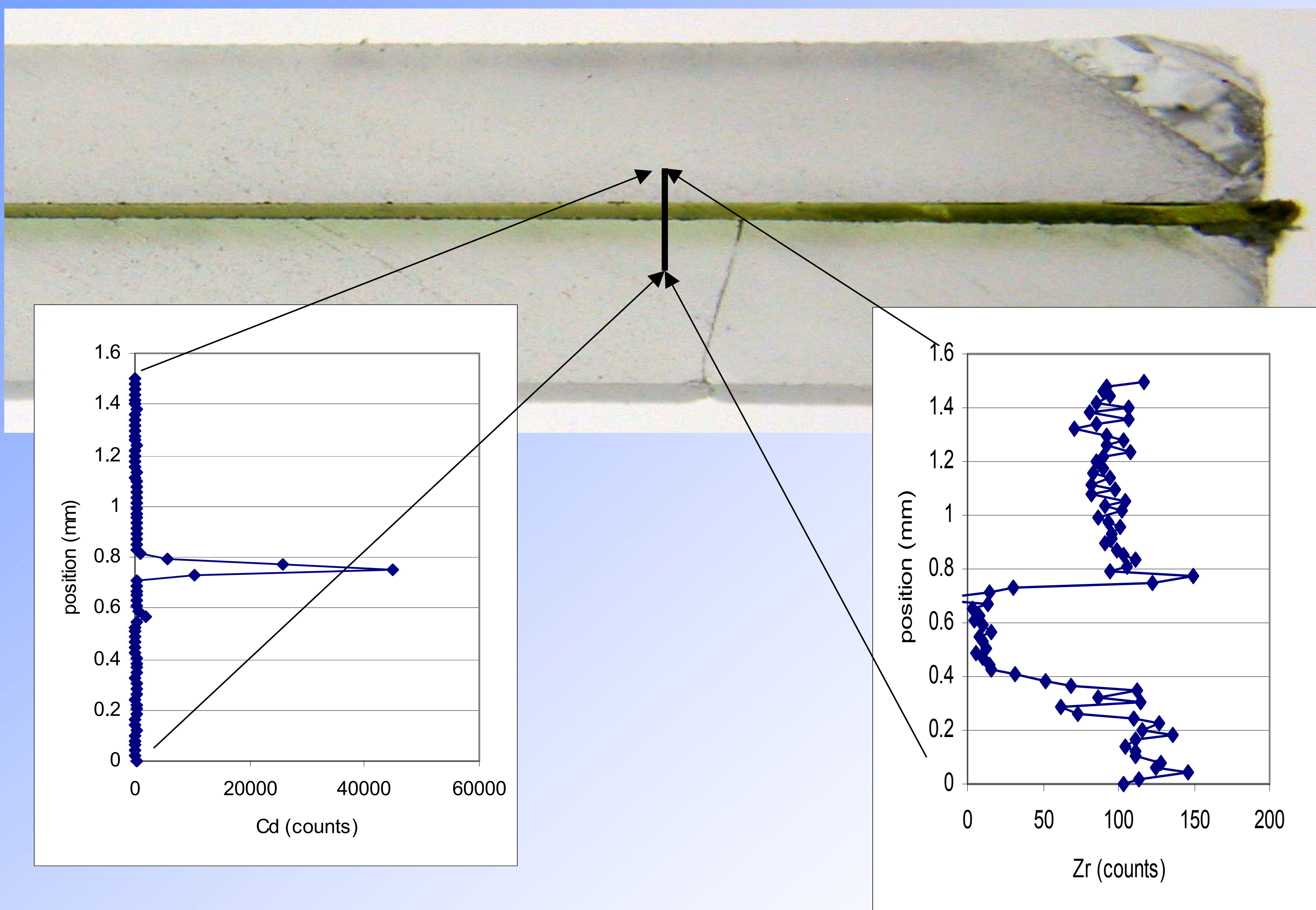
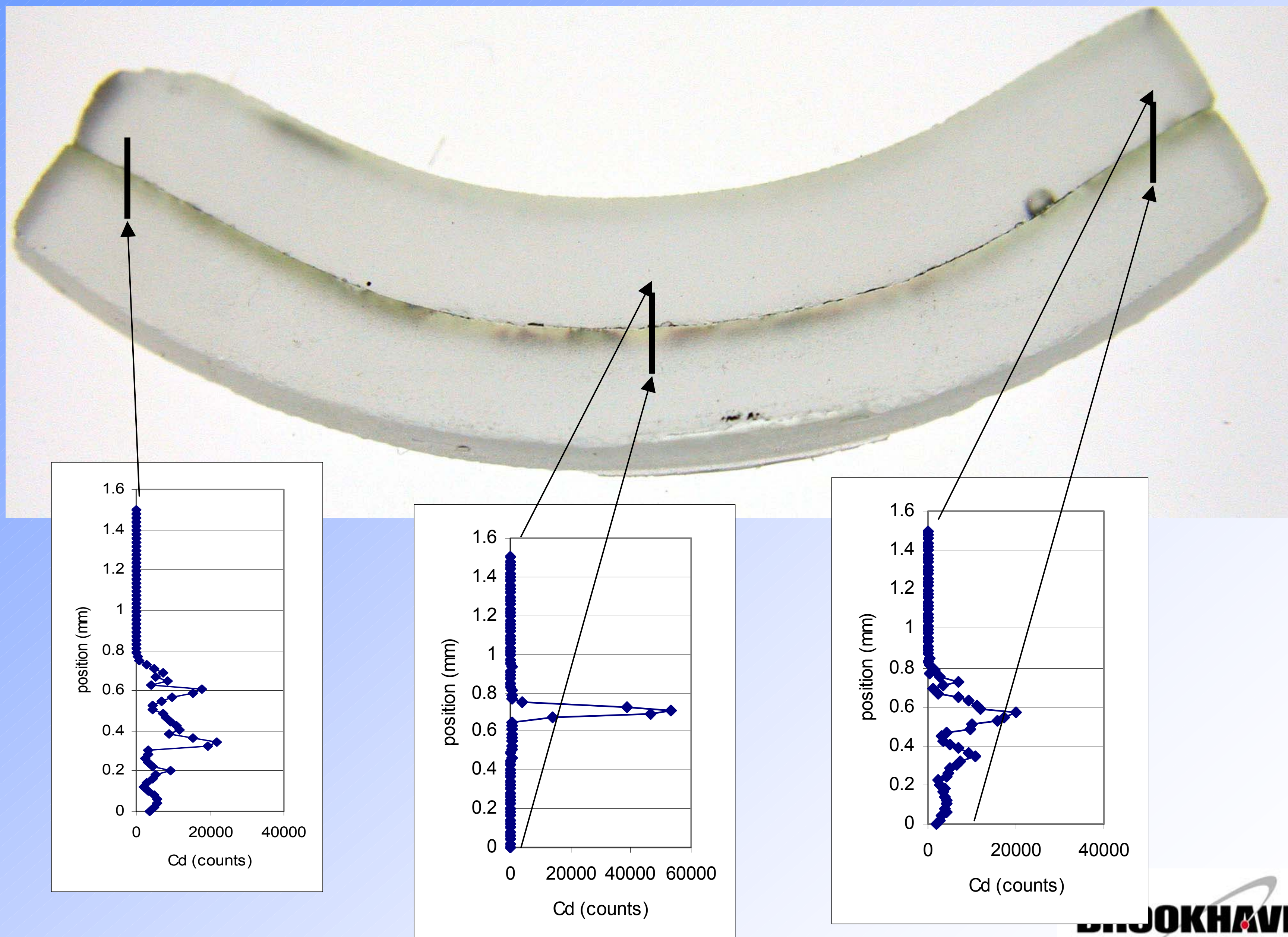
XRF-micro-probing -Cd & Zr Distribution in PV Glass Unheated Sample -Vertical Cross Section



XRF-micro-probe -Cd Distribution in PV Glass 760 °C, Section taken from middle of sample



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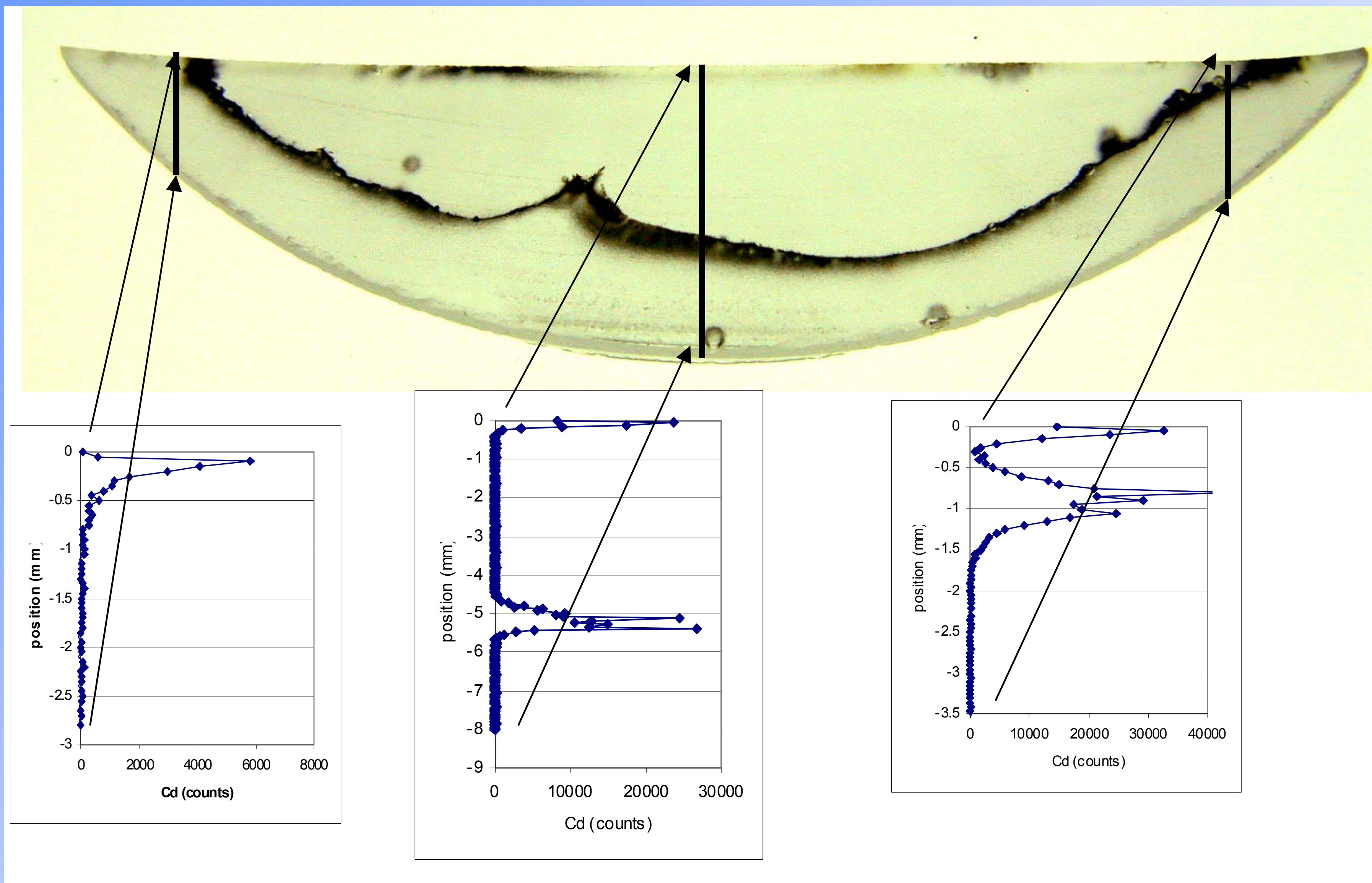
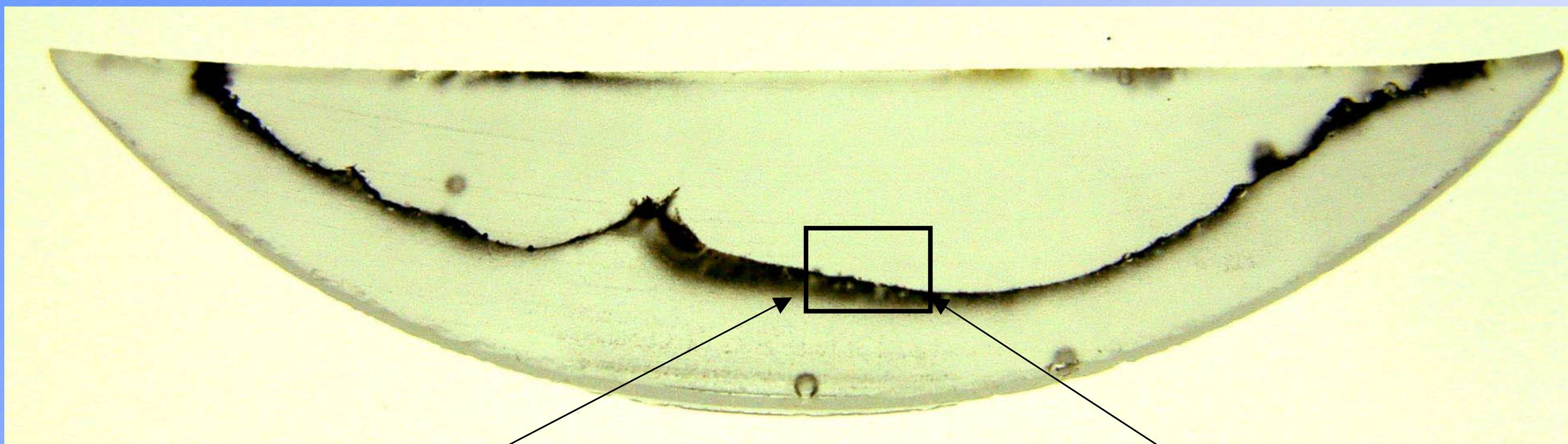
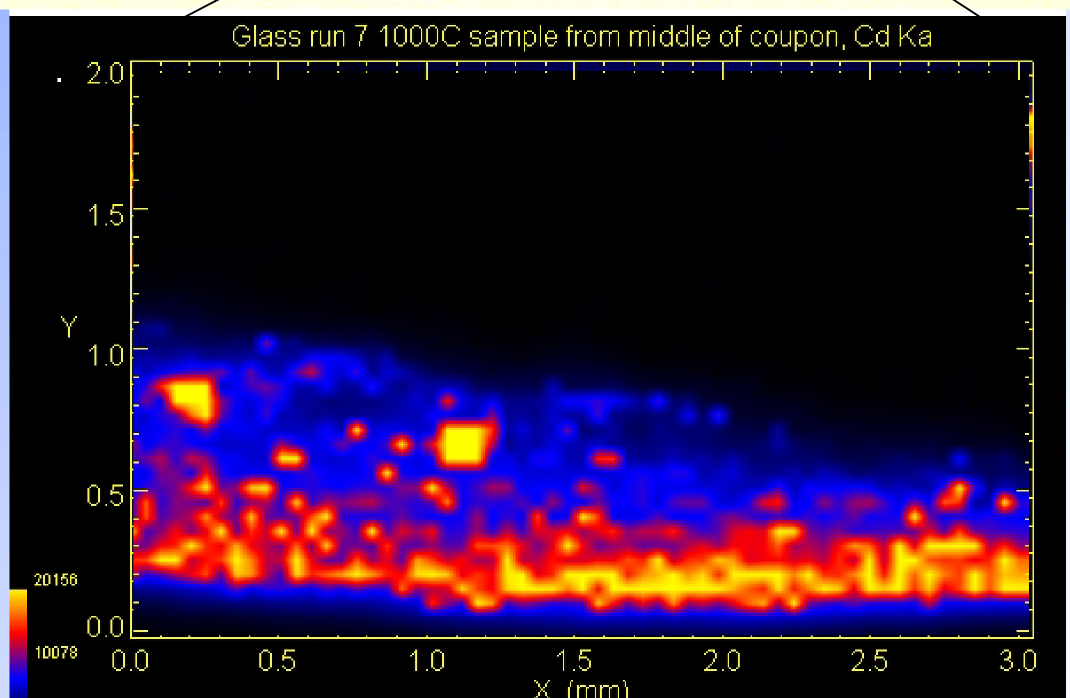
XRF-micro-probe -Cd Distribution in PV Glass

1000 °C, Section taken from middle of sample



XRF-micro-spectroscopy -Cd Mapping in PV Glass 1000 °C, Section taken from middle of sample





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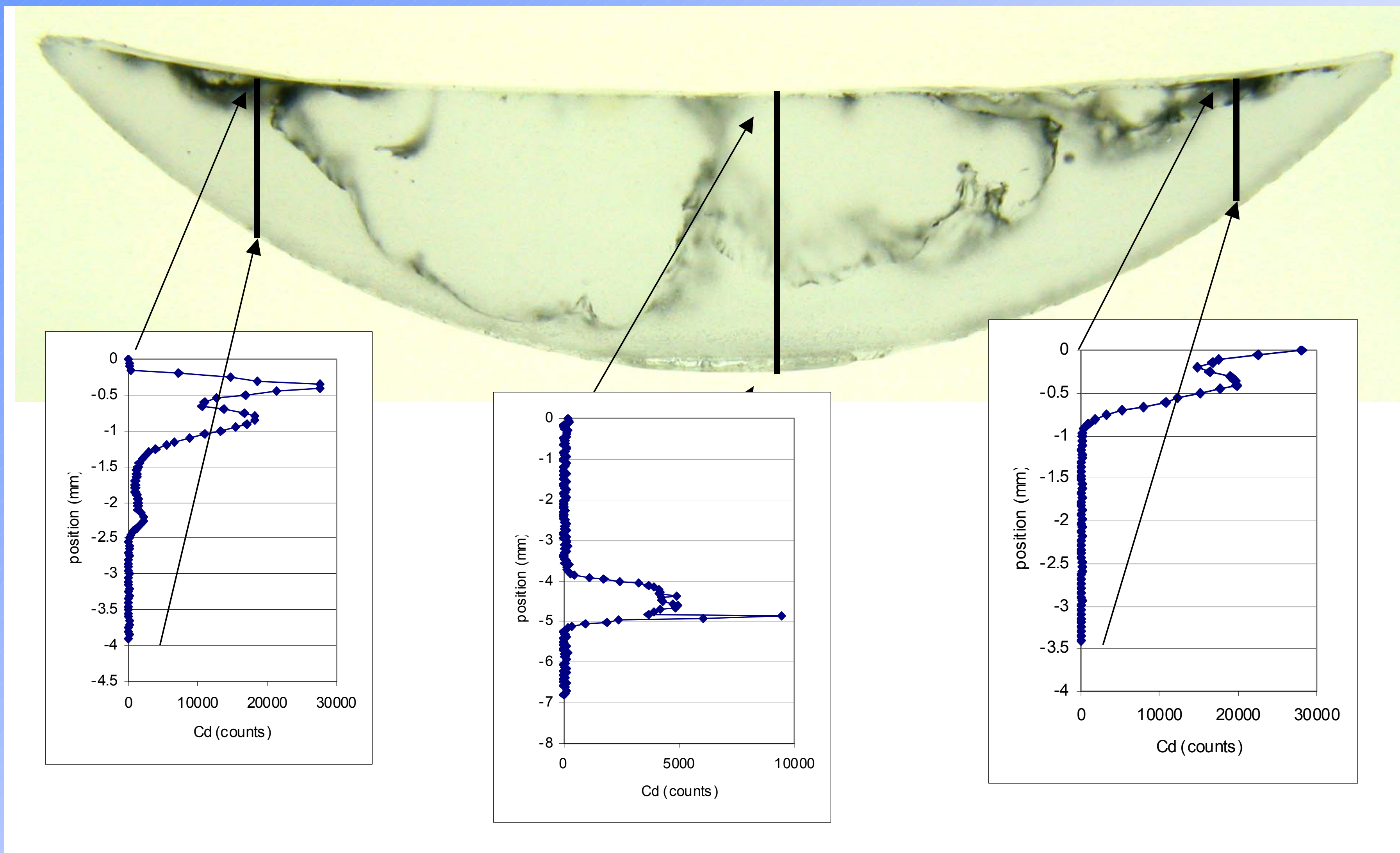
XRF-micro-probing -Cd Distribution in PV Glass
1000 °C, Section taken from right side of sample



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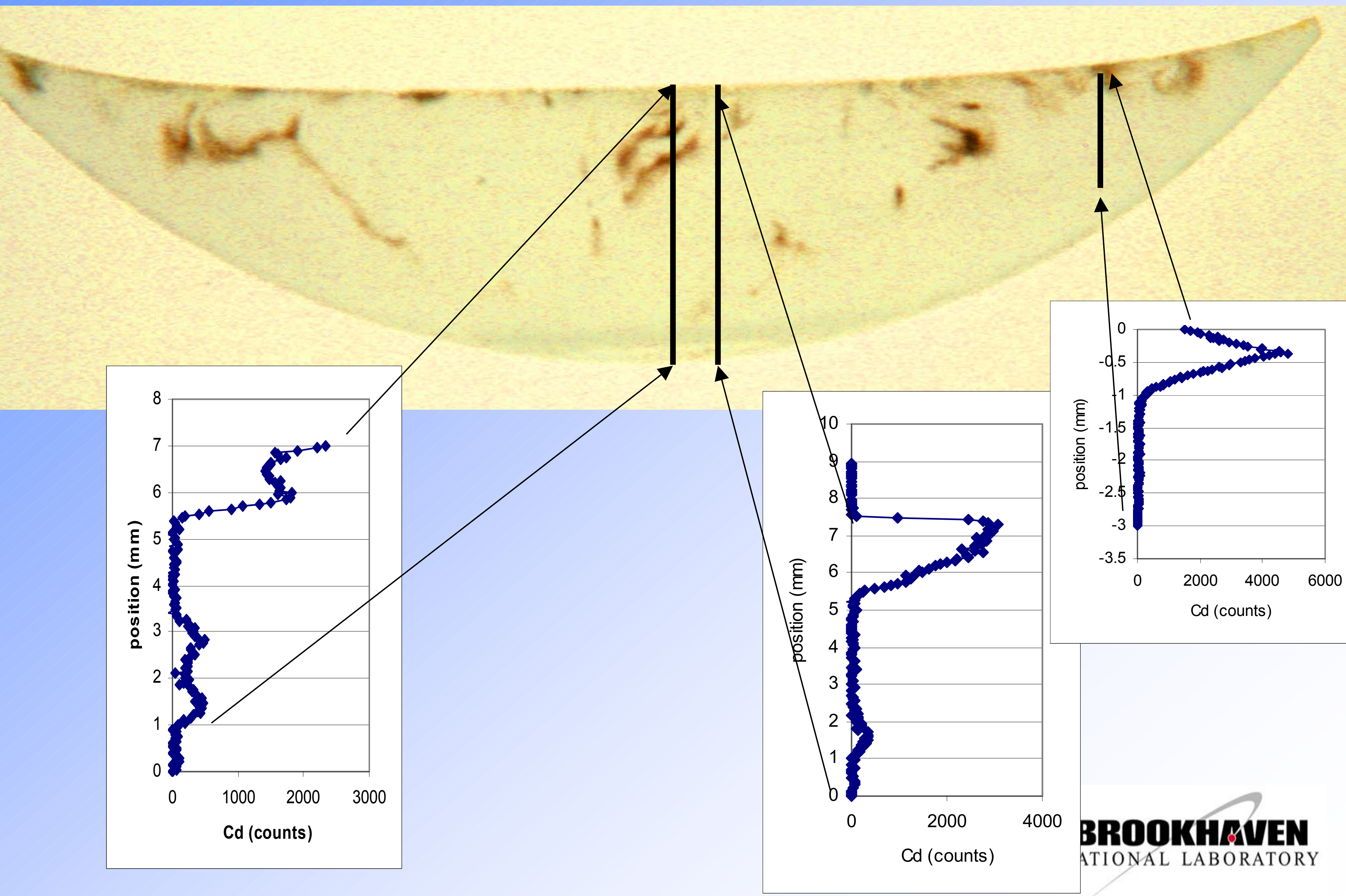
XRF-micro-probing -Cd Distribution in PV Glass 1100 °C, Section taken from middle of sample



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Decommisioning of end-of-life CdTe PV modules

- Concerns about leaching from PV disposed in municipal landfills
- This issue is not unique to CdTe PV
  - TCLP –US-EPA
  - DEV -Germany
  - STLC and TTLC –California HWCL
- Concerns about PV modules in MW incinerators,
- Recycling will resolve these concerns
- Recycling is technically feasible and cost is not excessive

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Atmospheric Cd emissions from the Life-Cycle of CdTe PV Modules –Reference Case

Process	Air Emissions (g Cd/ton Cd*)	Allocation (%)	Air Emissions (mg Cd/GWh)
1. Mining of Zn ores	2.7	0.58	0.02
2. Zn Smelting/Refining	40	0.58	0.30
3. Cd purification	6	100	7.79
4. CdTe Production	6	100	7.79
5. CdTe PV Manufacturing	3	100	3.90
TOTAL EMISSIONS			19.80
*ton of Cd used in manufacturing			

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Atmospheric Cd emissions from the Life-Cycle of CdTe PV Modules –Worst Case

Process	Air Emissions (g Cd/ton Cd*)	Allocation (%)	Air Emissions (mg Cd/GWh)
1. Mining of Zn ores	27	0.58	0.29
2. Zn Smelting/Refining	1000	0.58	10.76
3. Cd purification	12	100	22.26
4. CdTe Production	12	100	22.26
5. CdTe PV Manufacturing	6	100	11.13
TOTAL EMISSIONS			66.71
*ton of Cd used in manufacturing			

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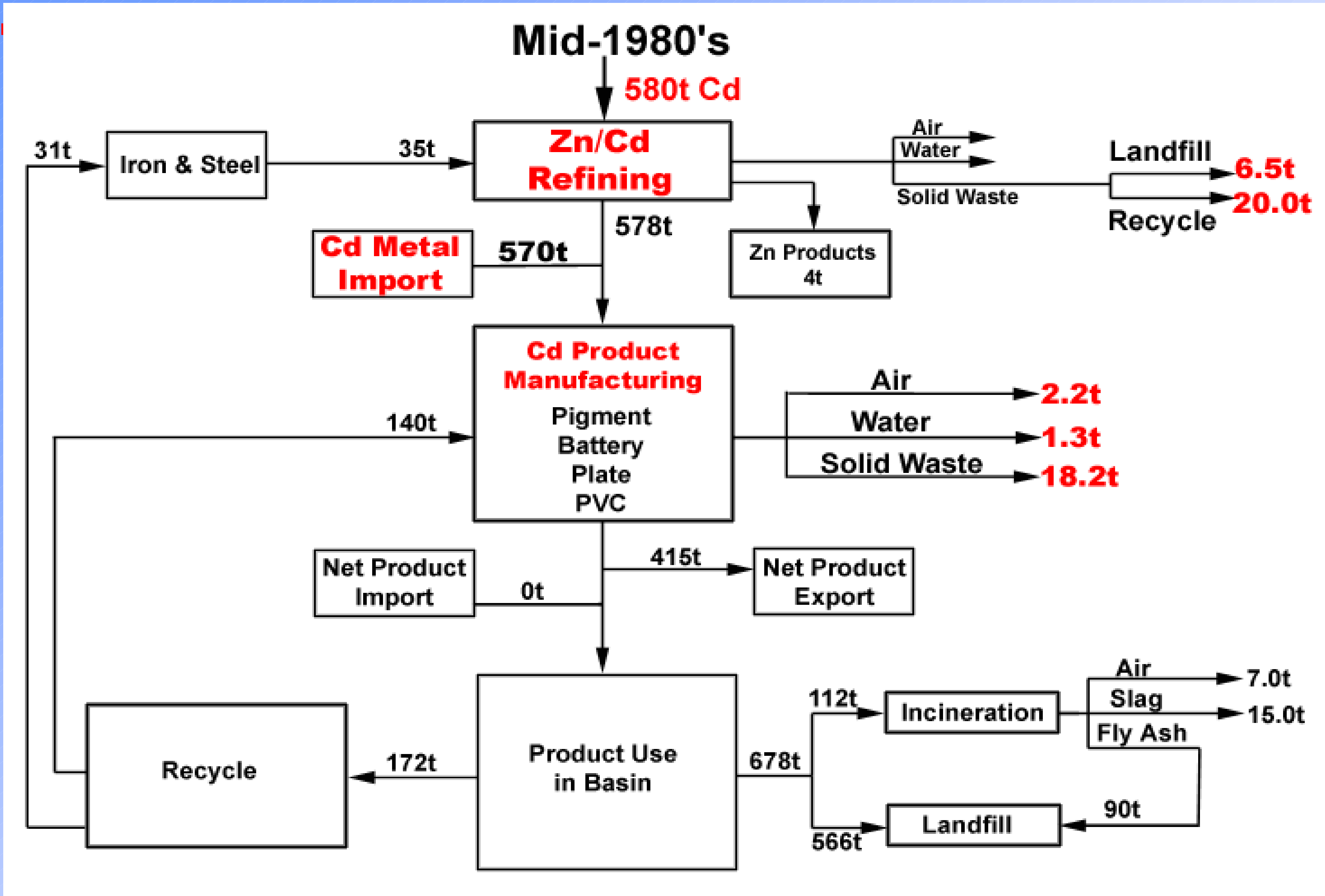
Cd Use in CdTe PV Production

Cd is produced as a byproduct of Zn production
and can either be put to **beneficial uses** or **discharged** into the environment

- Above statement is supported by:
  - US Bureau of Mines reports
  - Rhine Basin study (the largest application of Systems Analysis on Industrial Metabolism)

Cd Flow in the Rhine Basin



Source: Stigliani & Anderberg, Chapter 7, Industrial Metabolism, The UN University, 1994

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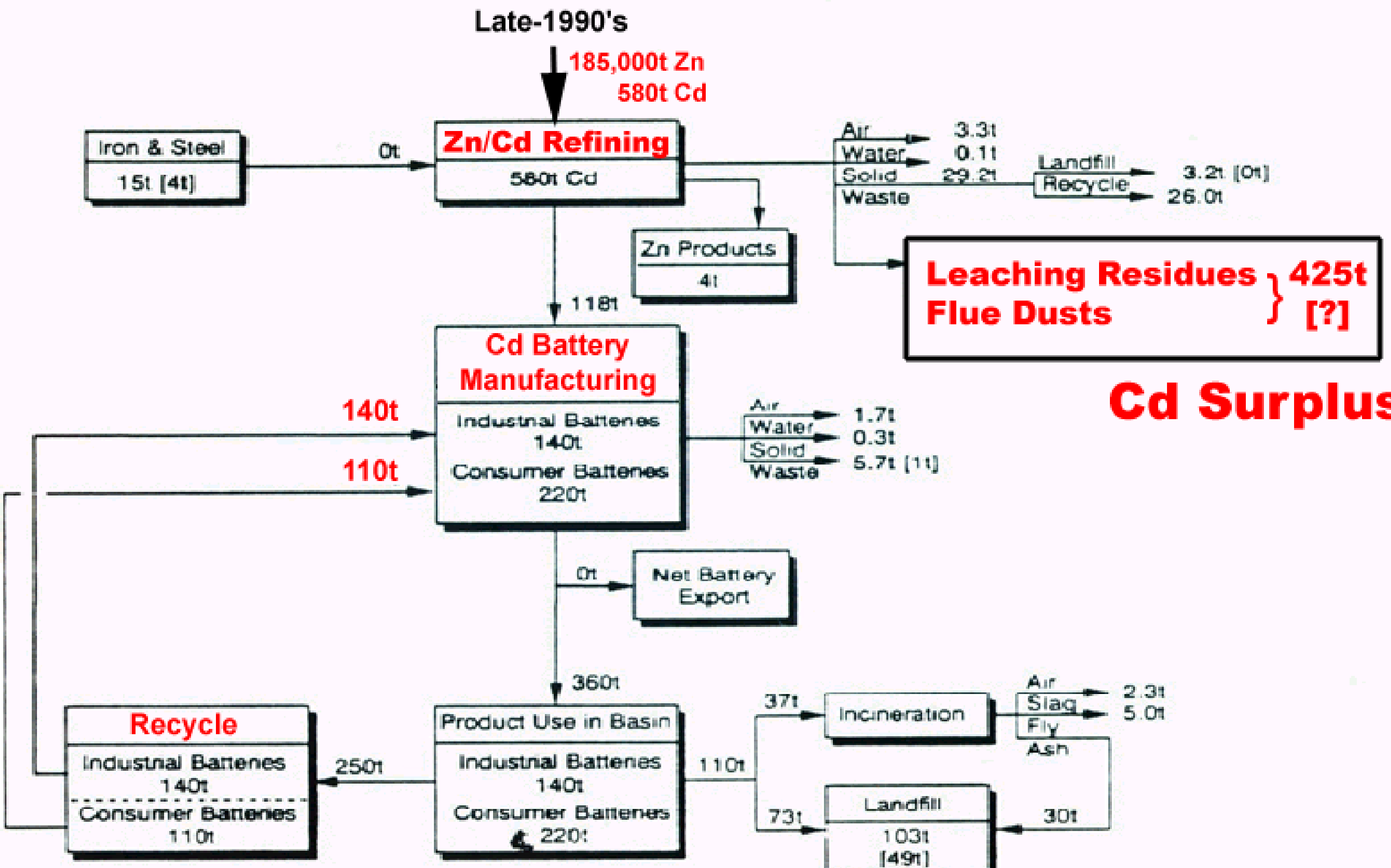
Rhine Basin: Cd Banning Scenario



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Source: Stigliani & Anderberg, Chapter 7, Industrial Metabolism, The UN University, 1994

Cd Use & Disposal in the Rhine Basin: The effect of banning Cd products

"So, the ultimate effect of banning Cd products and recycling 50% of disposed consumer batteries may be to shift the pollution load from the product disposal phase to the Zn/Cd production phase. This does not imply that banning Cd-containing products is not a wise strategy; rather, it indicates that if such a ban were to be implemented, special provisions would have to be made for the safe handling of surplus Cd wastes generated at the Zn refineries!

One possible option would be to allow the production and use of Cd-containing products with inherently low availability for leaching. The other option, depositing the Cd-containing wastes in safely contained landfills, has other risks"

Source: Stigliani & Anderberg, Chapter 7, Industrial Metabolism, The United Nations University, 1994

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Cd vs. CdTe PV

Compound	$T_{melting}$ (°C)	$T_{boiling}$ (°C)	Solubility (g/100 cc)	Toxic/ Carcinogen
Cd	321	765	insoluble	yes
$Cd(OH)_2$	300	-	2.6e-04	yes
CdTe	1041	-	insoluble	?

• CdTe is much more stable than Cd and $Cd(OH)_2$ used in batteries

• In addition, CdTe in PV is encapsulated between glass sheets

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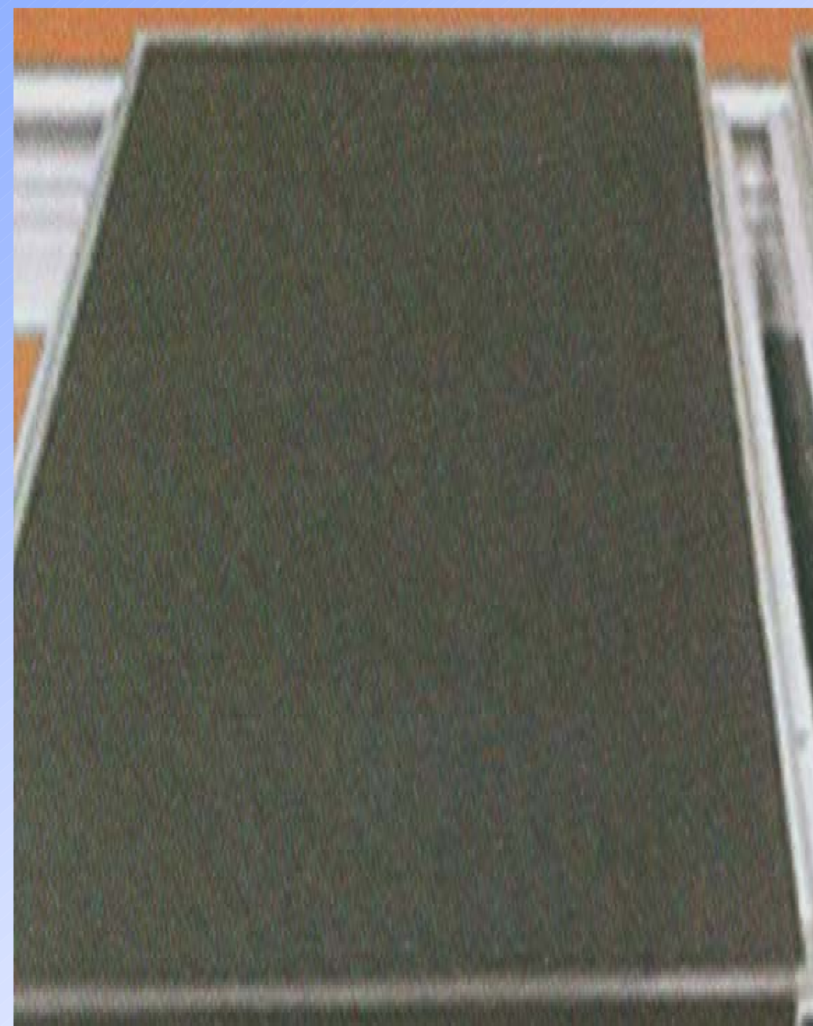
NiCd Battery to CdTe PV Comparisons

10 g Cd / C-size



7 g Cd/m^2

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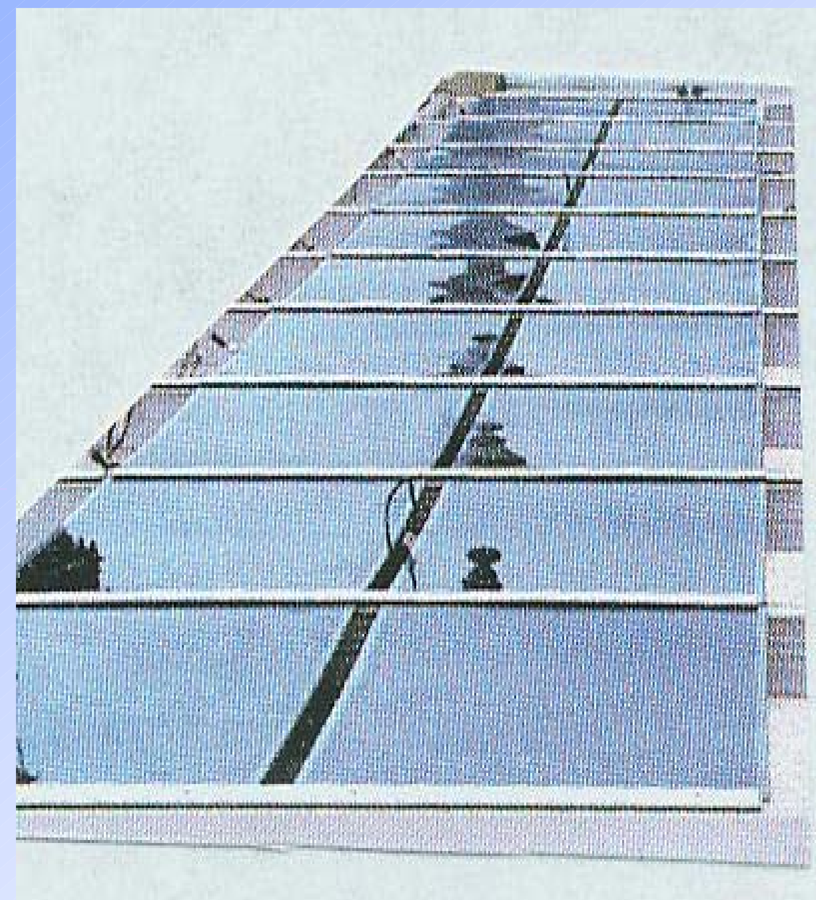
NiCd Battery to CdTe PV Comparisons

7 batteries = 70 g Cd = 1 kW CdTe PV

3265 kg Cd/GWh



1.3 kg Cd/GWh

- **Cd in CdTe PV generates 2,500 times more electricity than NiCd batteries**

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Cd from Coal-burning Power Plants

- Cd Air Emissions
  - 2 g/GWh (median); 7.2 g/GWh (average) *(EPRI database)*
    - Assuming Cd Removal of 98.6% in ESPs
    - Cd in coal: 0.5 ppm (median); 1.8 ppm (average)
- Cd Fine Dust
  - 140 g/GWh
- Other Emissions
  - CO_2: 1000 ton/GWh
  - SO_2: 8 ton/GWh
  - NOx: 3 ton/GWh
  - PM_{10}: 0.4 ton/GWh
  - Mercury, Arsenic, Dioxins, etc

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Conclusions

- Cd is produced as a byproduct of Zn production and can either be put to *beneficial* uses or *discharged* into the environment
- CdTe in PV is much safer than other current Cd uses
- CdTe PV uses Cd 2500 times more efficiently than NiCd batteries
- Air emissions of Cd from the Life Cycle of CdTe PV are 100-360 times lower than Cd emitted into air from coal power plants that PV replaces

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