Stone Soup – Immobilization of Radionuclides and Contaminants In Soil By Thermal Treatment

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Research Question of a Recent EMSP Project on Thermal Treatment of Concrete

- How does the extractability or leachability of the major DOE radionuclide contaminants (Cs, Sr,, Co, and U) change after concrete is heated through its range of strength deterioration up to its vitrification?

Concrete is a mixture of 20% hydrated Portland cement paste ($Ca(OH)_2$ & hydrated calcium silicates) and 80% inert aggregates (quartz, feldspar, or limestone sands and gravels).

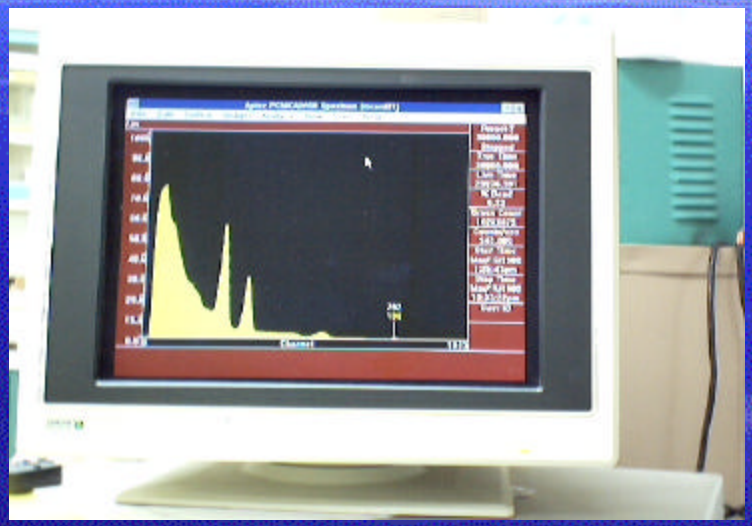
Assumptions (Biases) for Radionuclide Reactivity With Concrete During Heating

- Hydrated Portland cement paste is very reactive with Sr, Cs, Co, and U and its reactivity should change significantly when heated. Yes, that was found!
- Most common concrete aggregates will be relatively inert to radionuclides and will remain unreactive when heated. At ambient temperature, most were inert. But, when heated, all model aggregate materials (quartz, feldspar, and calcite) reacted strongly with radionuclides.

Heating and Extracting Soils - The Tools

Crucibles, Centrifuge Tubes, & Filter Units

Gamma Spectroscopy



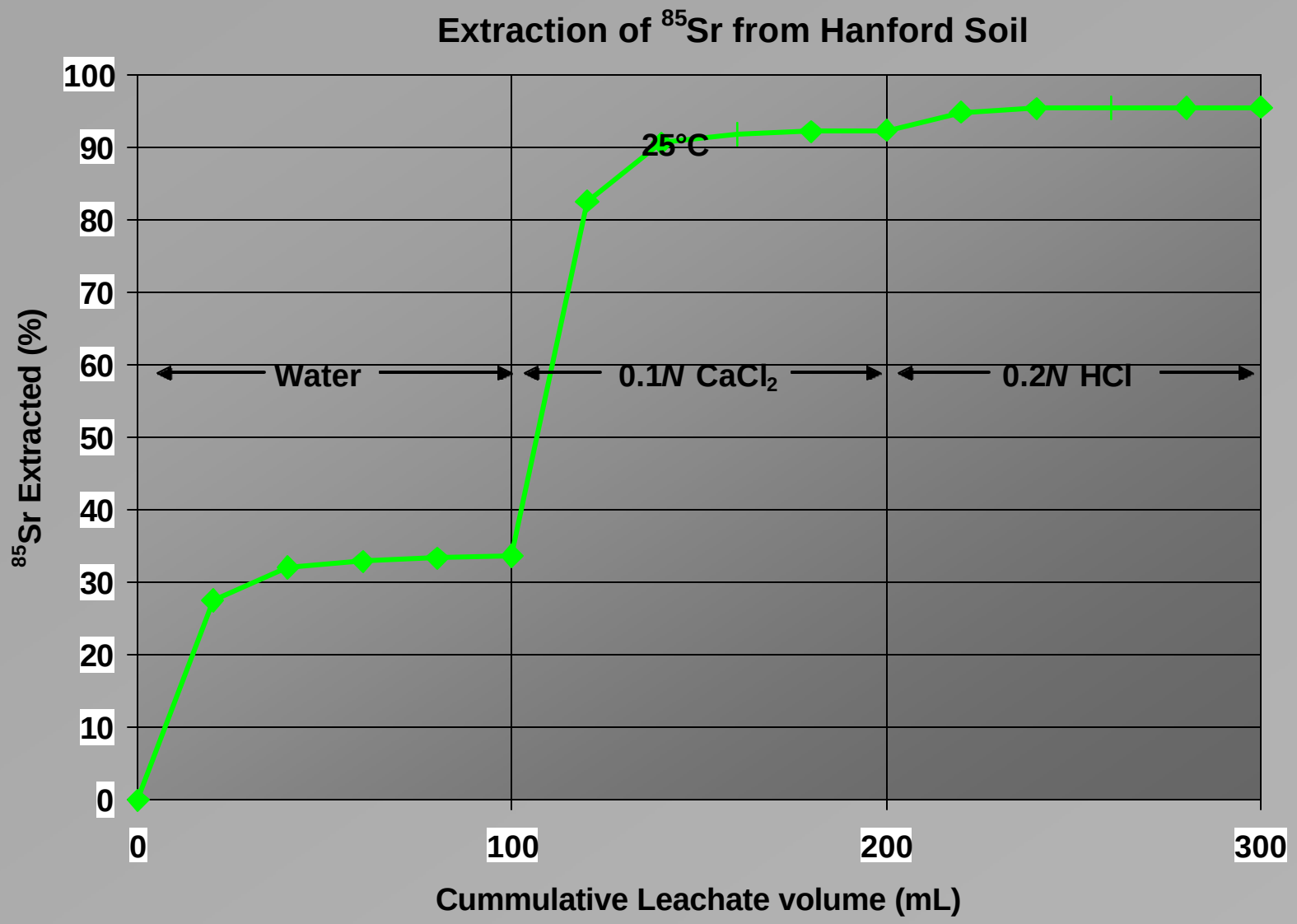
High-Temperature Furnace

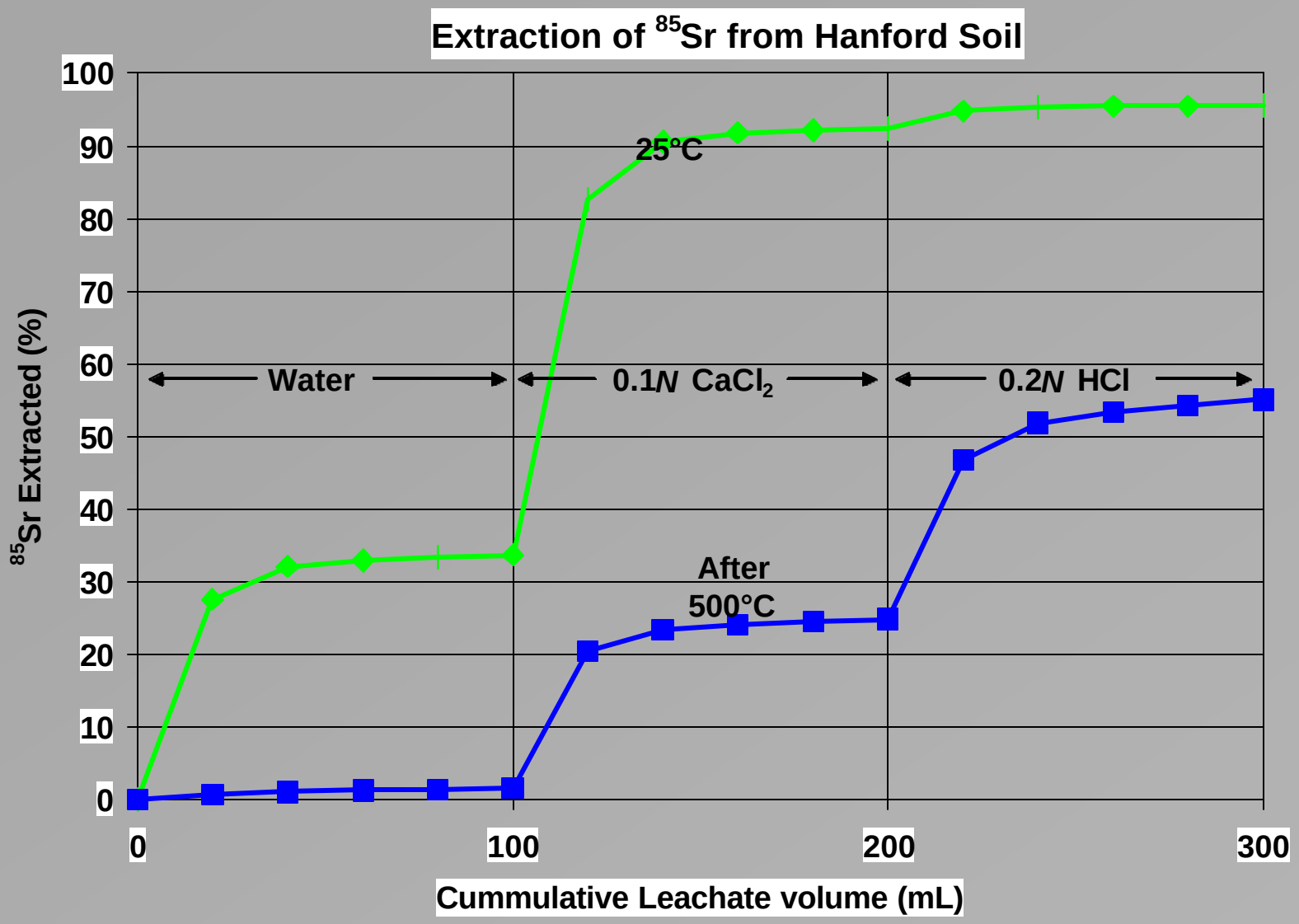
Thousands of Extract Vials

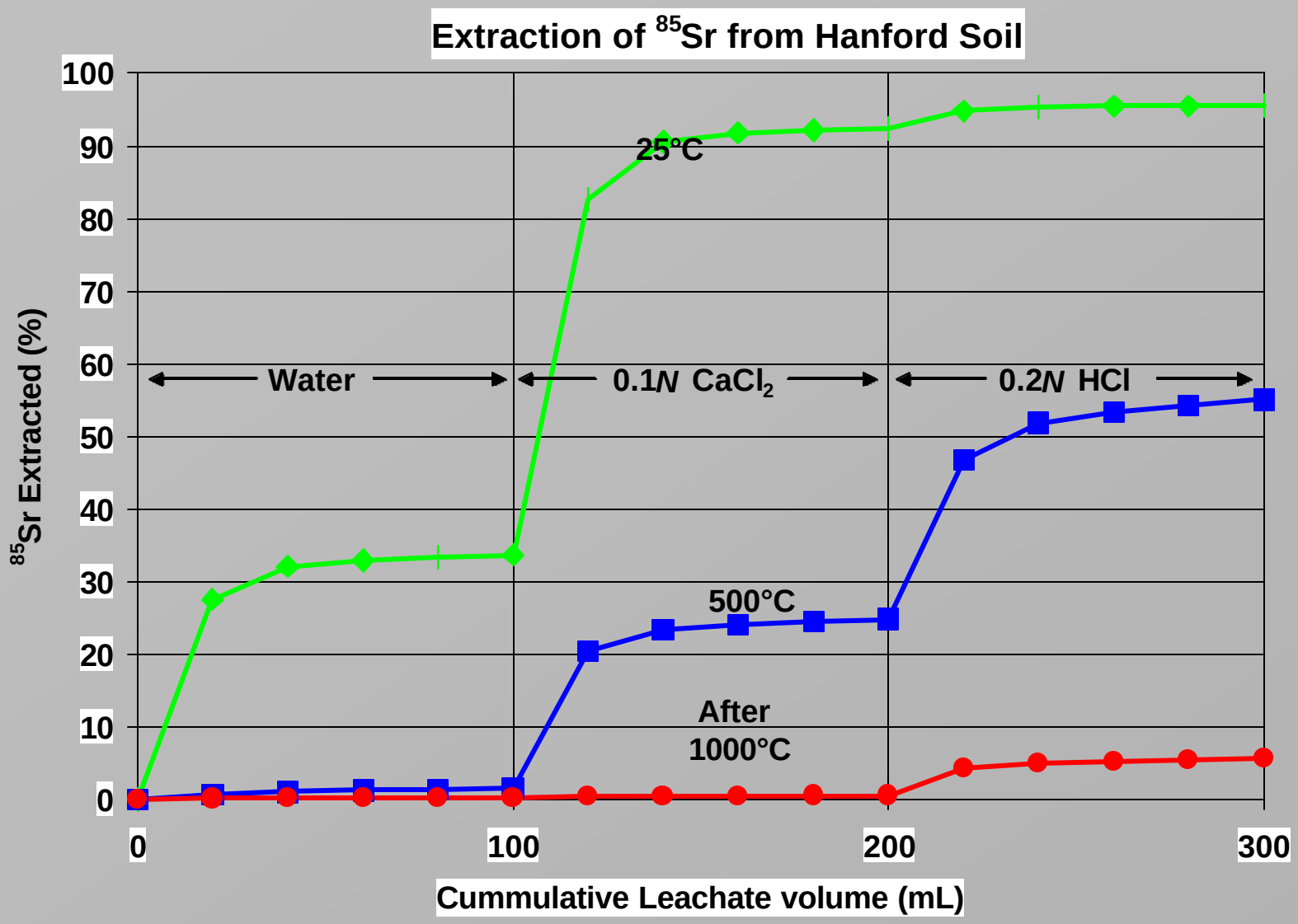
Sequential Extraction of Soil Samples

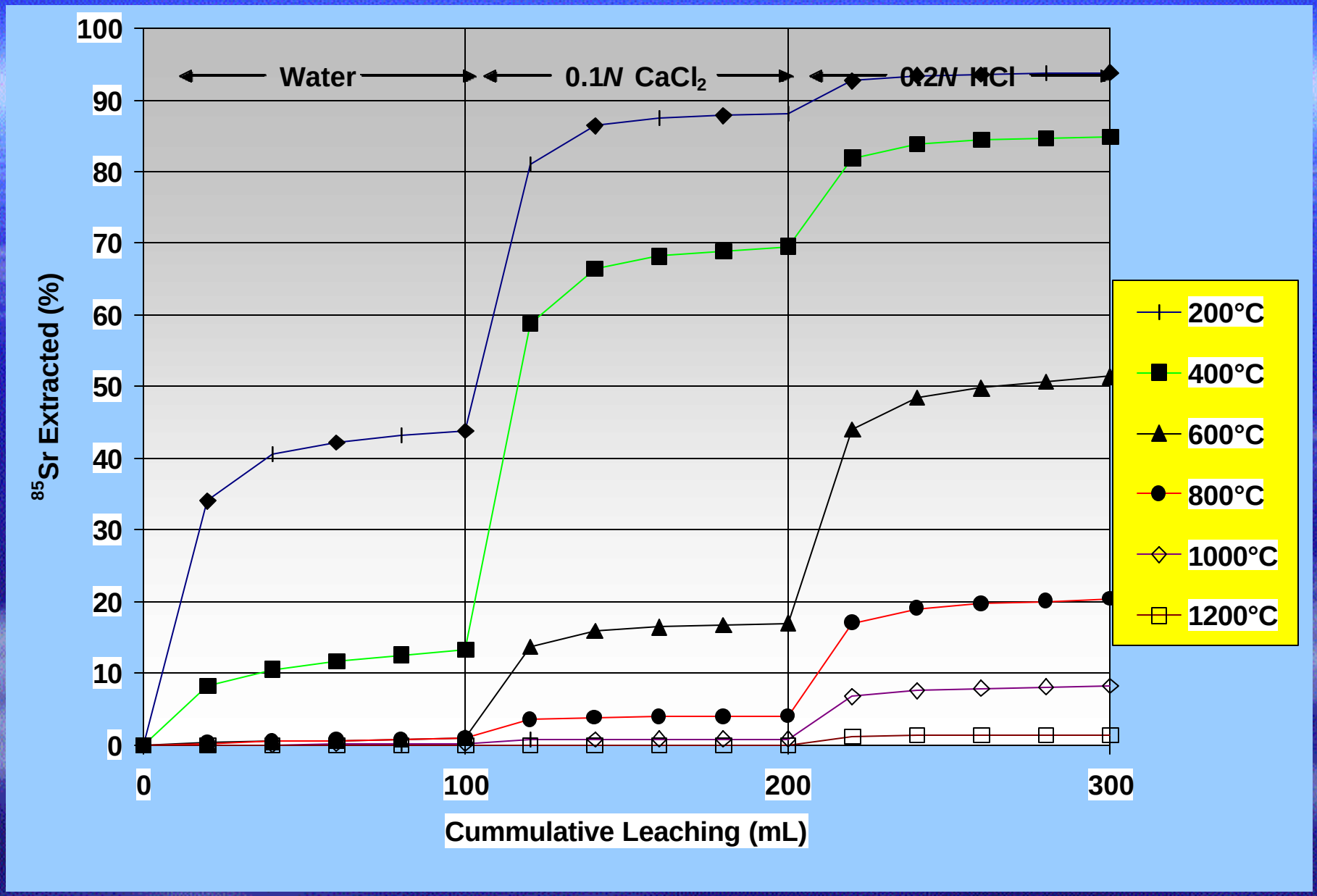
Soil and Concrete Sequential Extraction

- Concept – Extract soil with a sequence of reagents of increasing harshness to compare and make inferences about the mineral forms and environmental availability of contaminants or nutrients.
- Many sequential extraction protocols are popular. For example, water and dilute $MgCl_2$ (water soluble/exchangeable), ammonium acetate, pH4 (carbonates), hydroxylamine (Fe/Mn Oxides), H_2O_2 (organic matter), nitric acid (acid soluble), alkali fusion (residual).
- We have used a simple sequence but with an important difference – extract the sample with each reagent five times until both it and you are exhausted!
- Our sequence involves:
- water (for solubles and ambient cation exchangeables)
- 0.1 N $CaCl_2$ to 100 milliequivants/gram (cation exchageables)
- 0.2 N HCl to 200 milliquivalents/gram (acid solubles and sorbed species)
- Residual via non-destructive gamma spectroscopy (immobilized species)


Extraction of 85Sr from Hanford Soil
85Sr Extracted (%)
100
90
80
70
60
50
40
30
20
10
0
25°C
Water
0.1N CaCl2
0.2N HCl
0
100
200
300
Cummulative Leachate volume (mL)

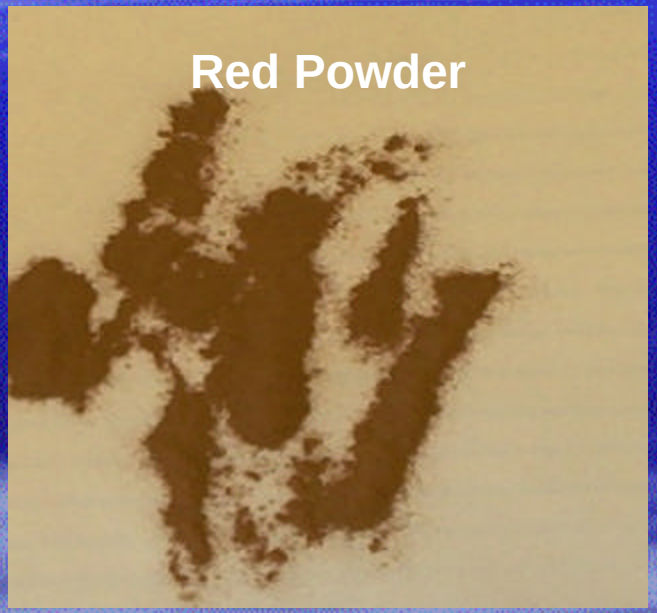

Extraction of 85Sr from Hanford Soil
85Sr Extracted (%)
100
90
80
70
60
50
40
30
20
10
0
Water
0.1N CaCl2
0.2N HCl
25°C
After
500°C
0
100
200
300
Cummulative Leachate volume (mL)


Extraction of ^{85}Sr from Hanford Soil
^{85}Sr Extracted (%)
100
90
80
70
60
50
40
30
20
10
0
Water
0.1*N* $CaCl_2$
0.2*N* HCl
25°C
500°C
After
1000°C
0
100
200
300
Cummulative Leachate volume (mL)

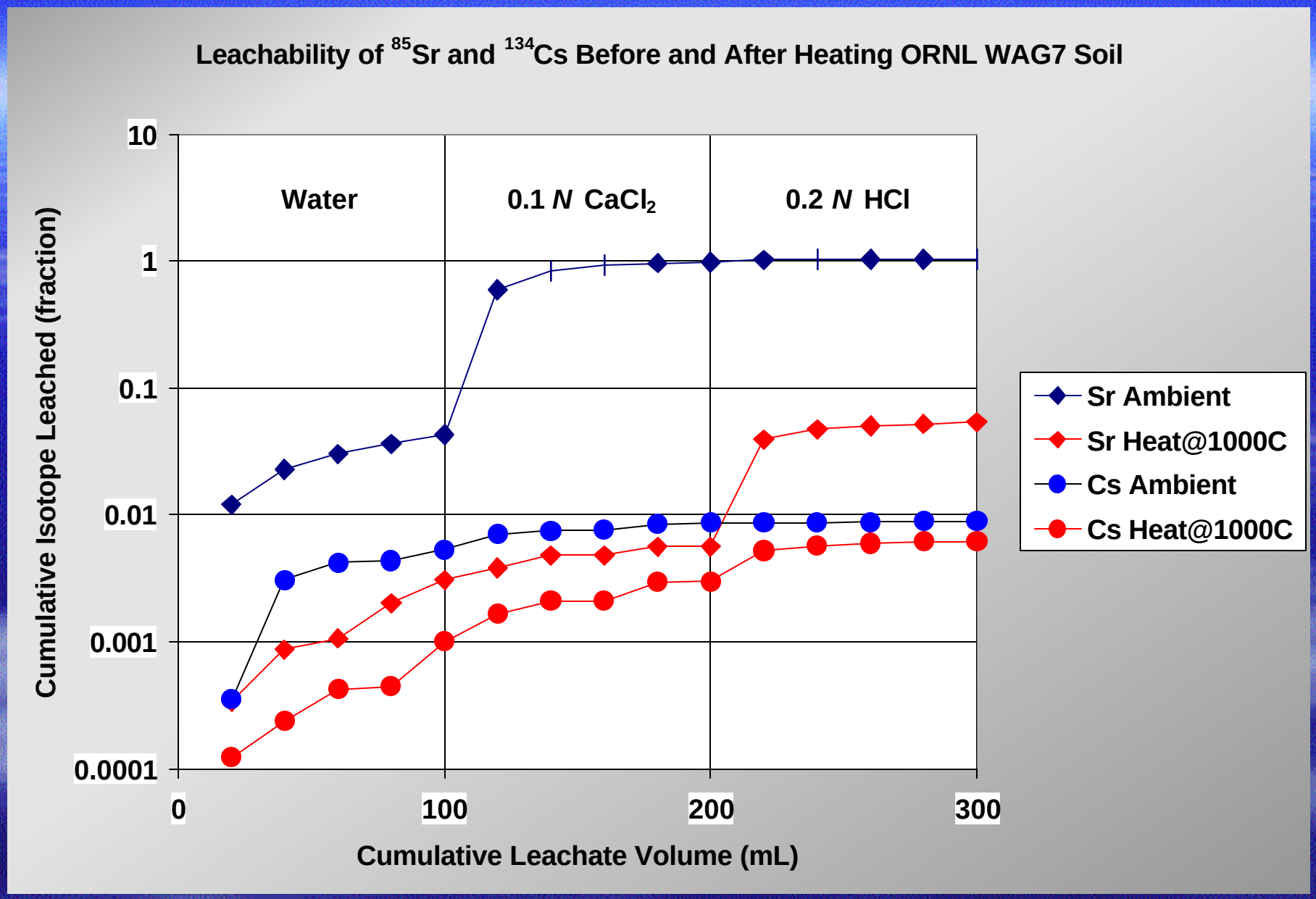

Water
0.1N CaCl2
0.2N KCl
85Sr Extracted (%)
Cummulative Leaching (mL)
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
200°C
400°C
600°C
800°C
1000°C
1200°C

Heating Melton Valley Soil - Visual Effects

1000°C

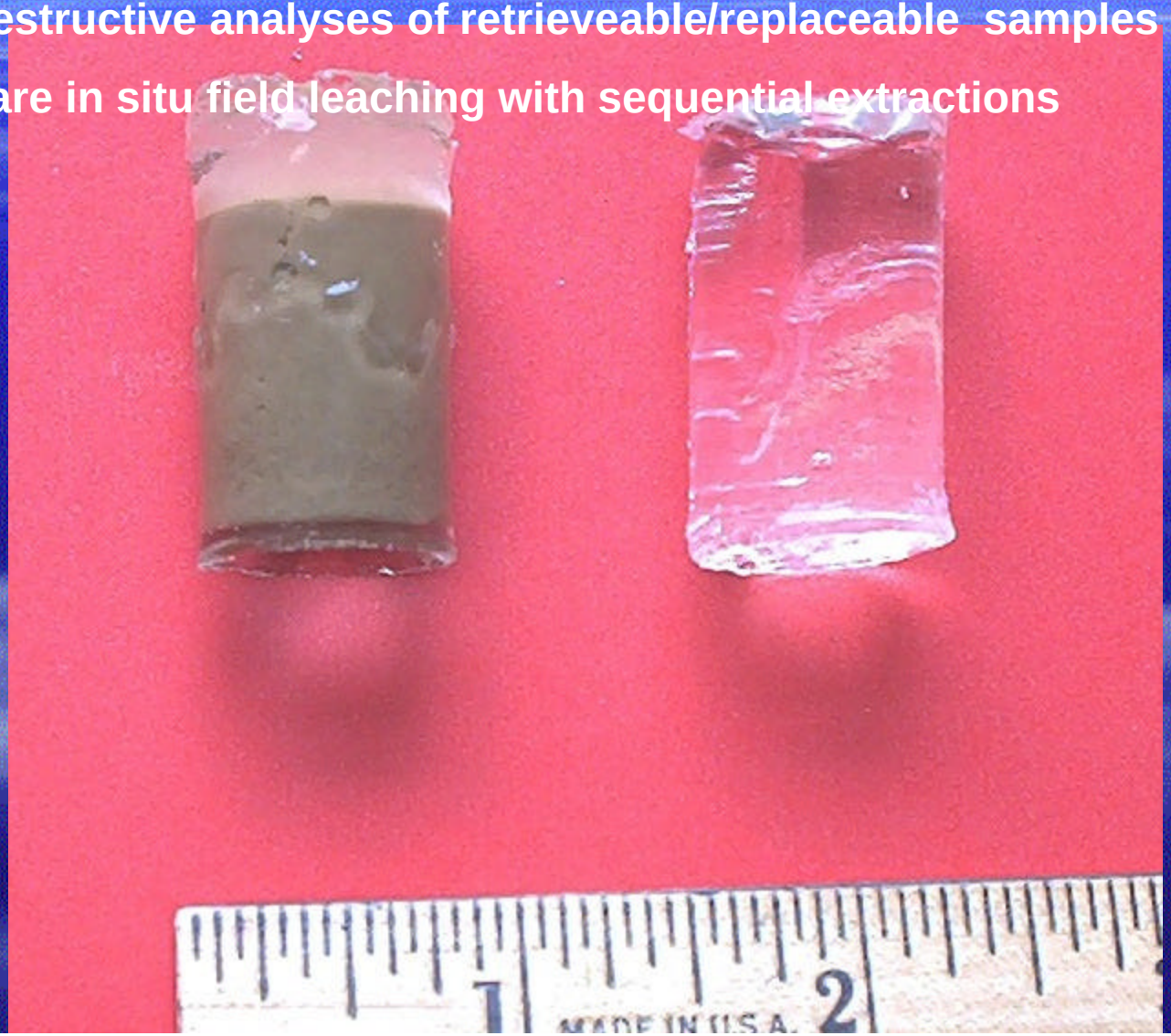


1500°C

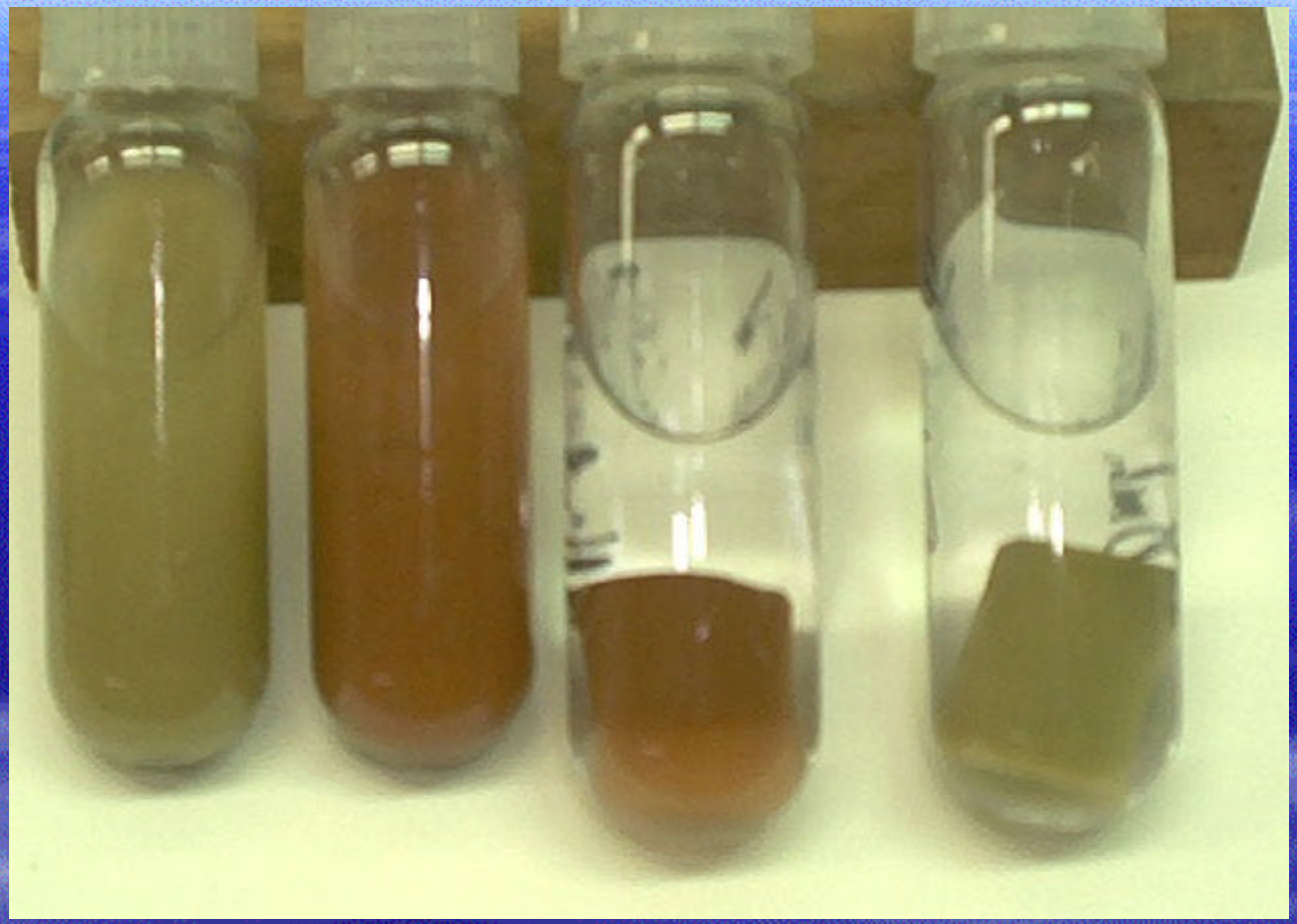

Leachability of 85Sr and 134Cs Before and After Heating ORNL WAG7 Soil
Water
0.1 N CaCl2
0.2 N HCl
10
1
0.1
0.01
0.001
0.0001
0
100
200
300
Cumulative Isotope Leached (fraction)
Cumulative Leachate Volume (mL)
Sr Ambient
Sr Heat@1000C
Cs Ambient
Cs Heat@1000C

PELCAPs (Permeable Environmental Leaching Capsules) – A way to leach test soils in situ in the field!

- **Polyacrylamide gel encapsulates spiked or treated soil but groundwater is free to permeate gel**
- **Non-destructive analyses of retrieveable/replaceable samples**
- **Compare in situ field leaching with sequential extractions**



Laboratory Sequential Extraction of Radioisotopes from “PELCAP”ped Soil

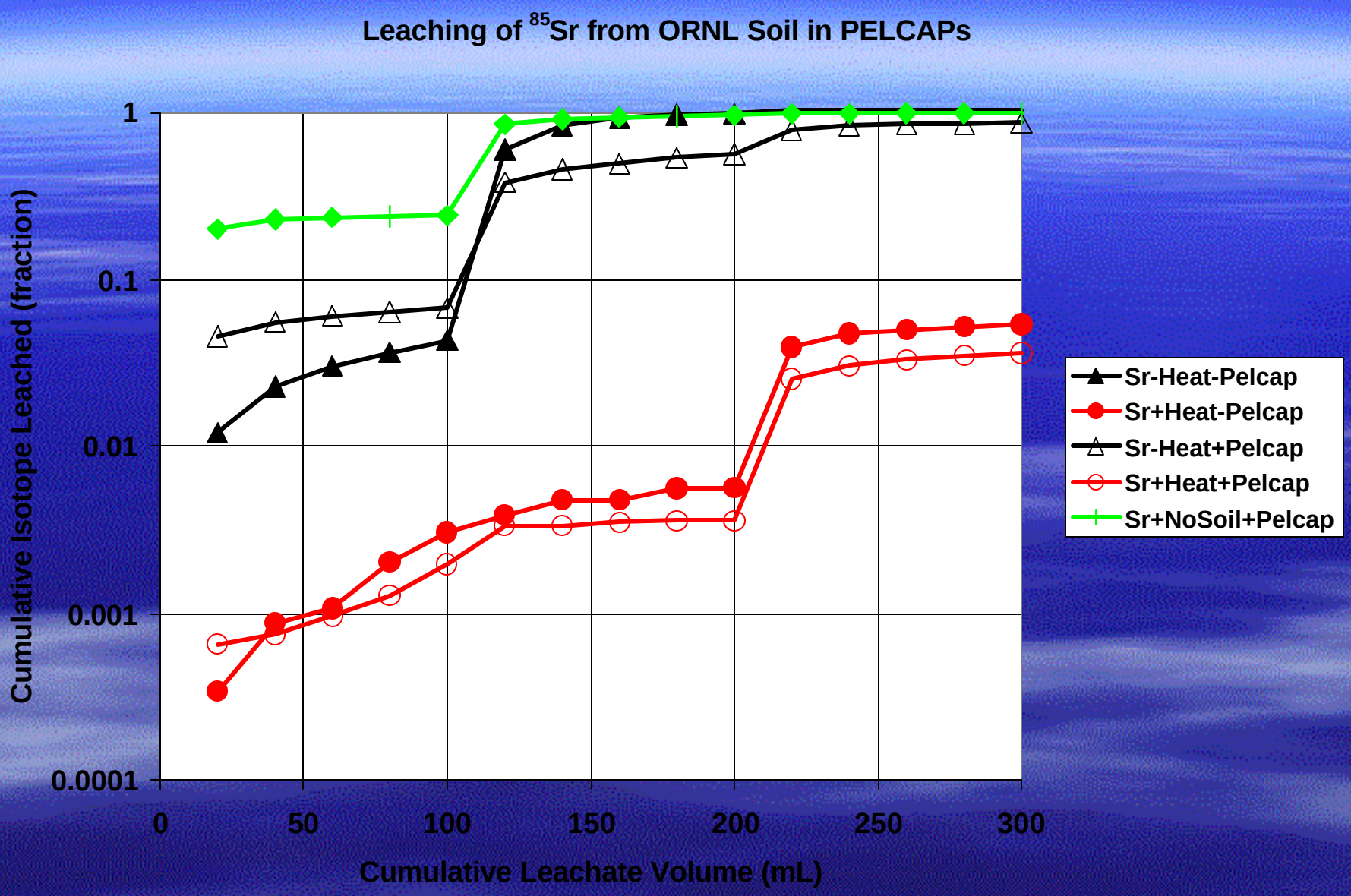


Unheated Soil

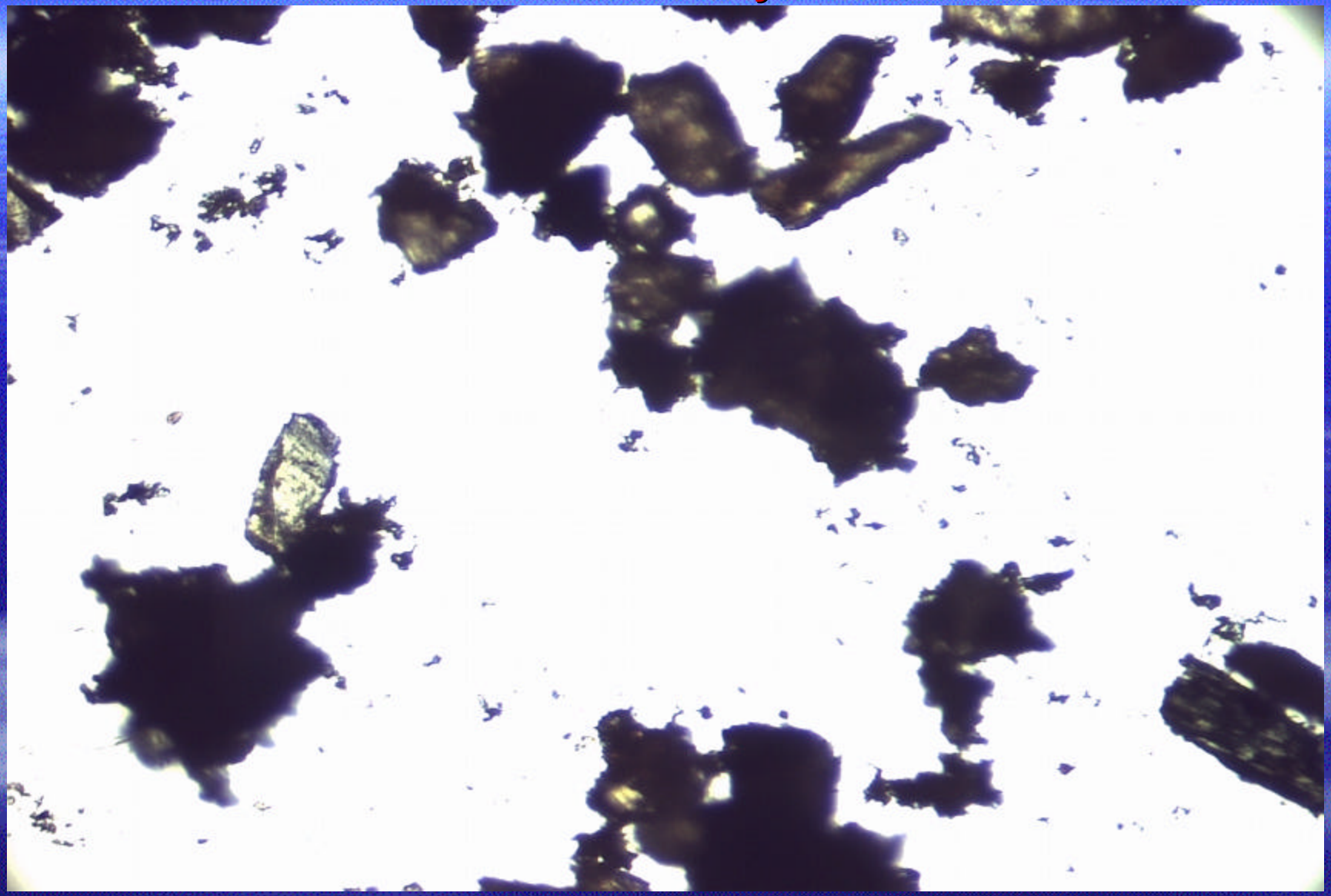
1000°C Soil

1000°C & PELCAP

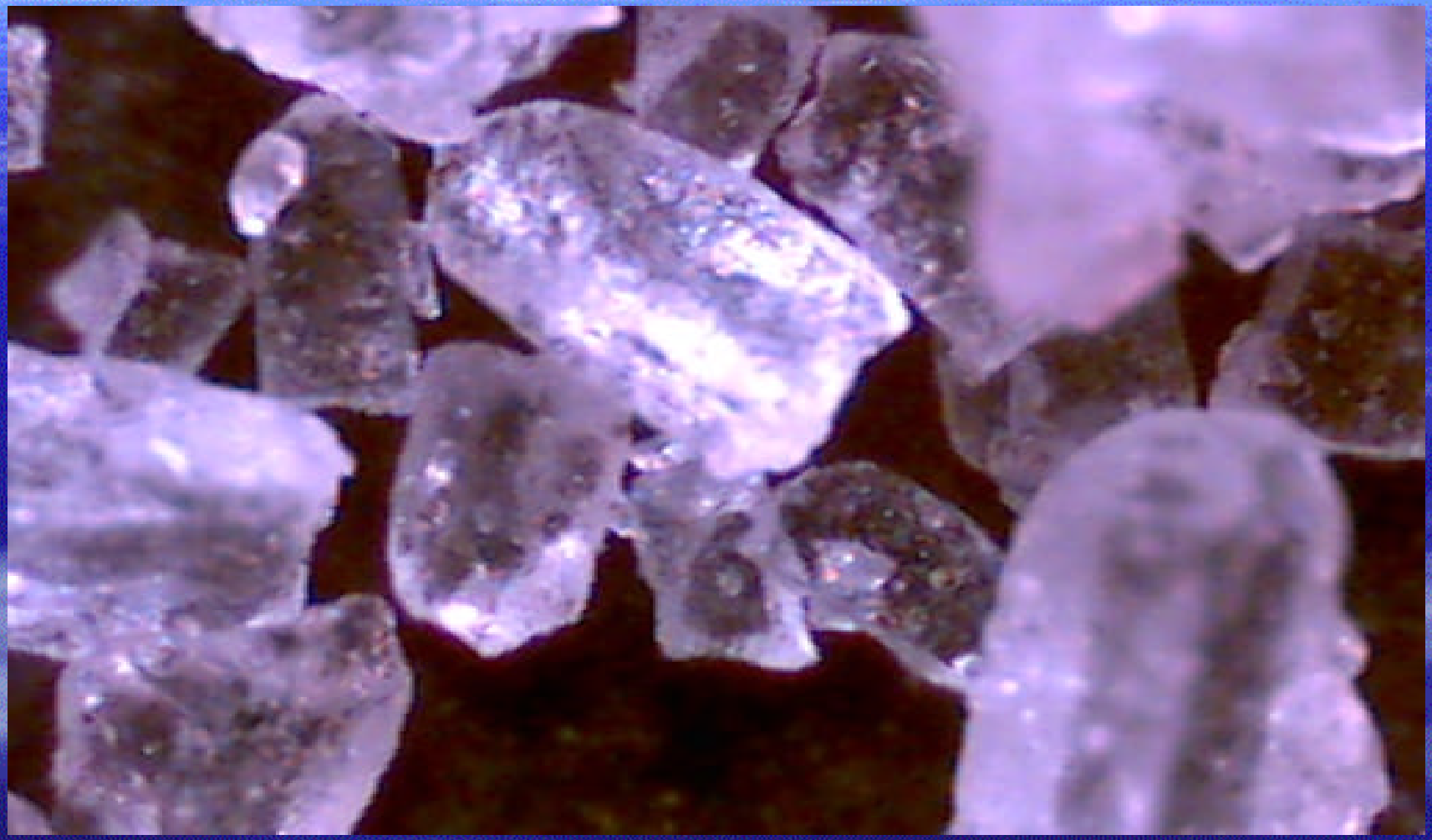
Unheated & PELCAP

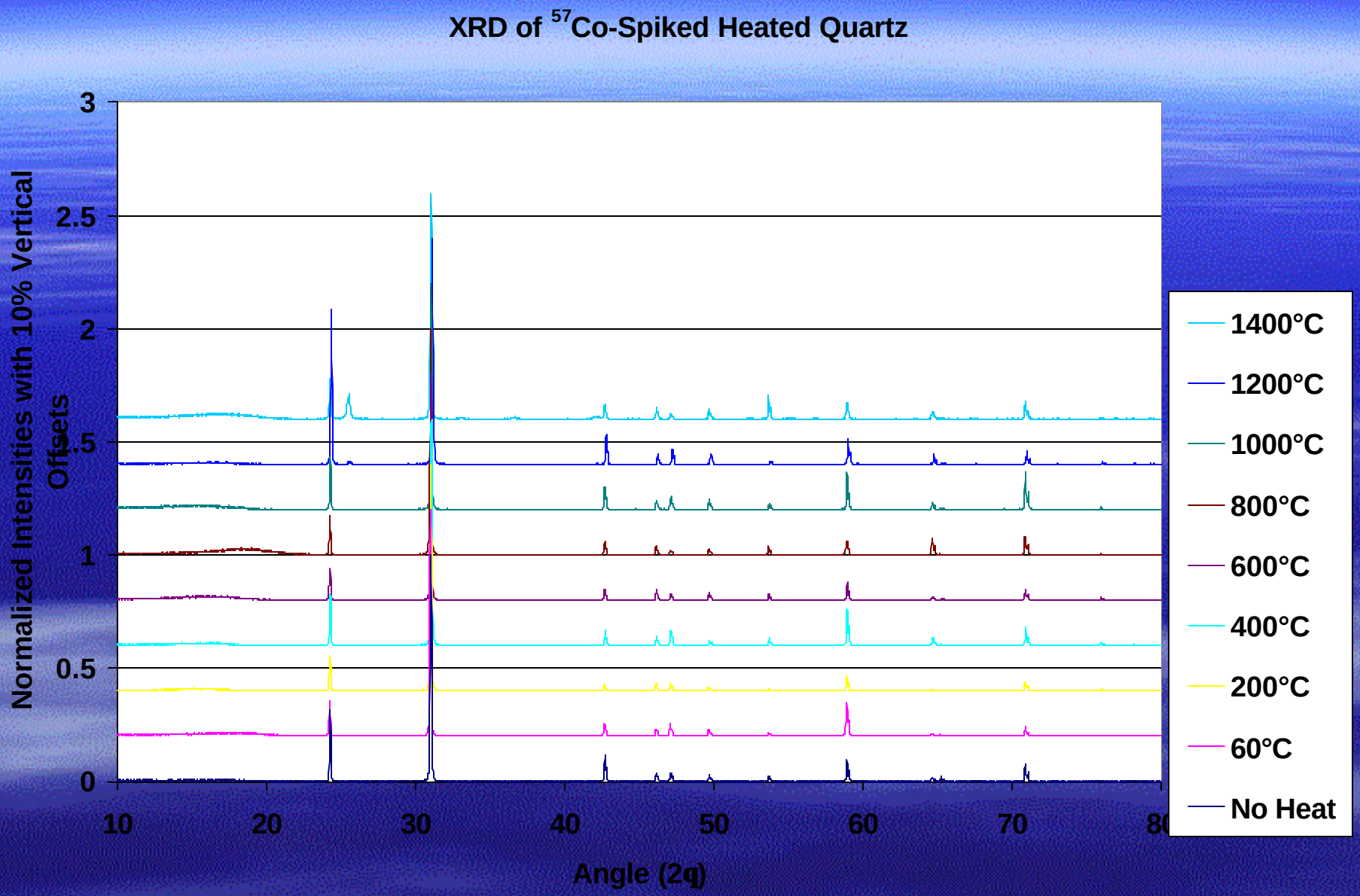

Leaching of 85Sr from ORNL Soil in PELCAPs
Cumulative Isotope Leached (fraction)
1
0.1
0.01
0.001
0.0001
0
50
100
150
200
250
300
Cumulative Leachate Volume (mL)
Sr-Heat-Pelcap
Sr+Heat-Pelcap
Sr-Heat+Pelcap
Sr+Heat+Pelcap
Sr+NoSoil+Pelcap

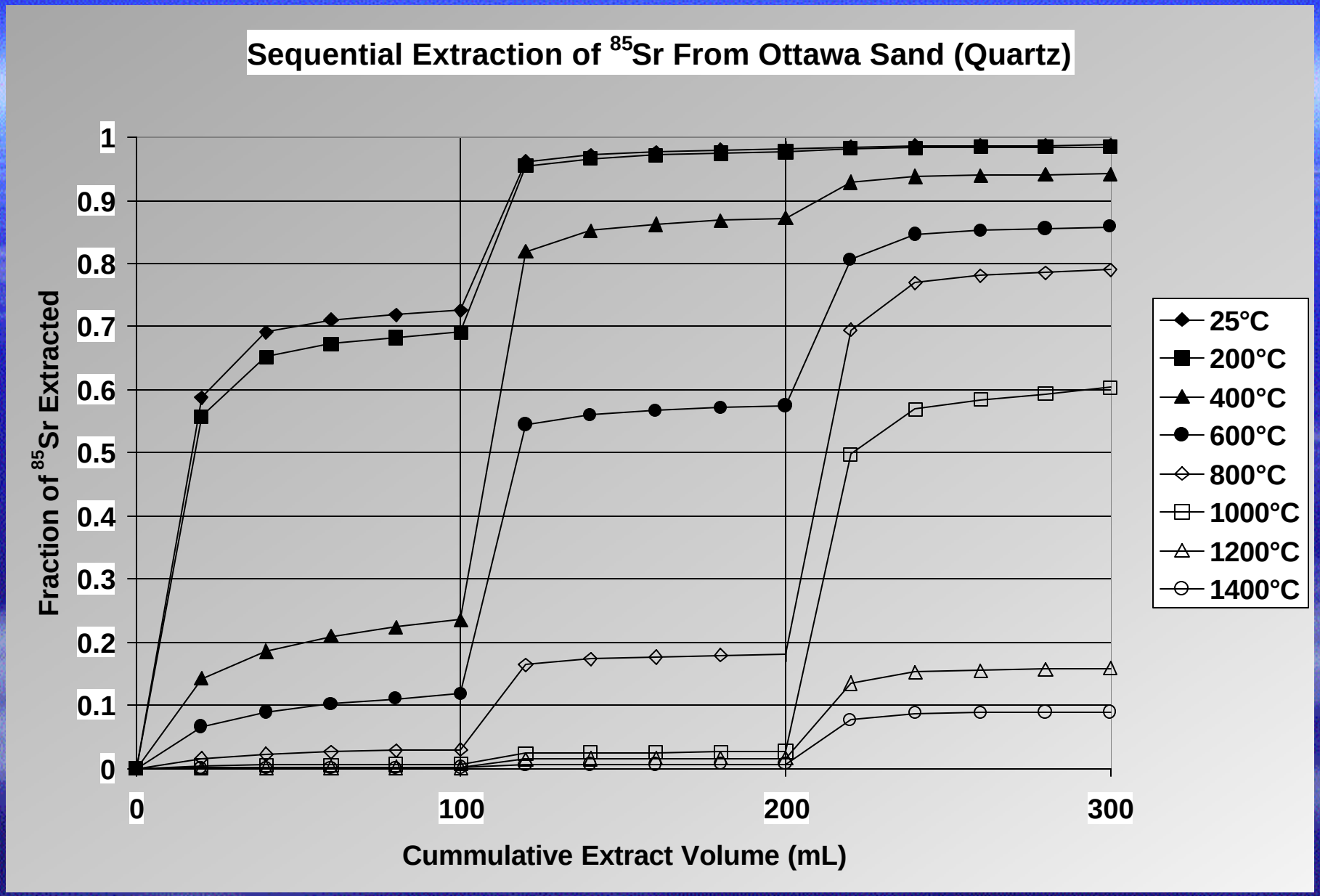
Hanford Sandy Soil



Quartz Grains

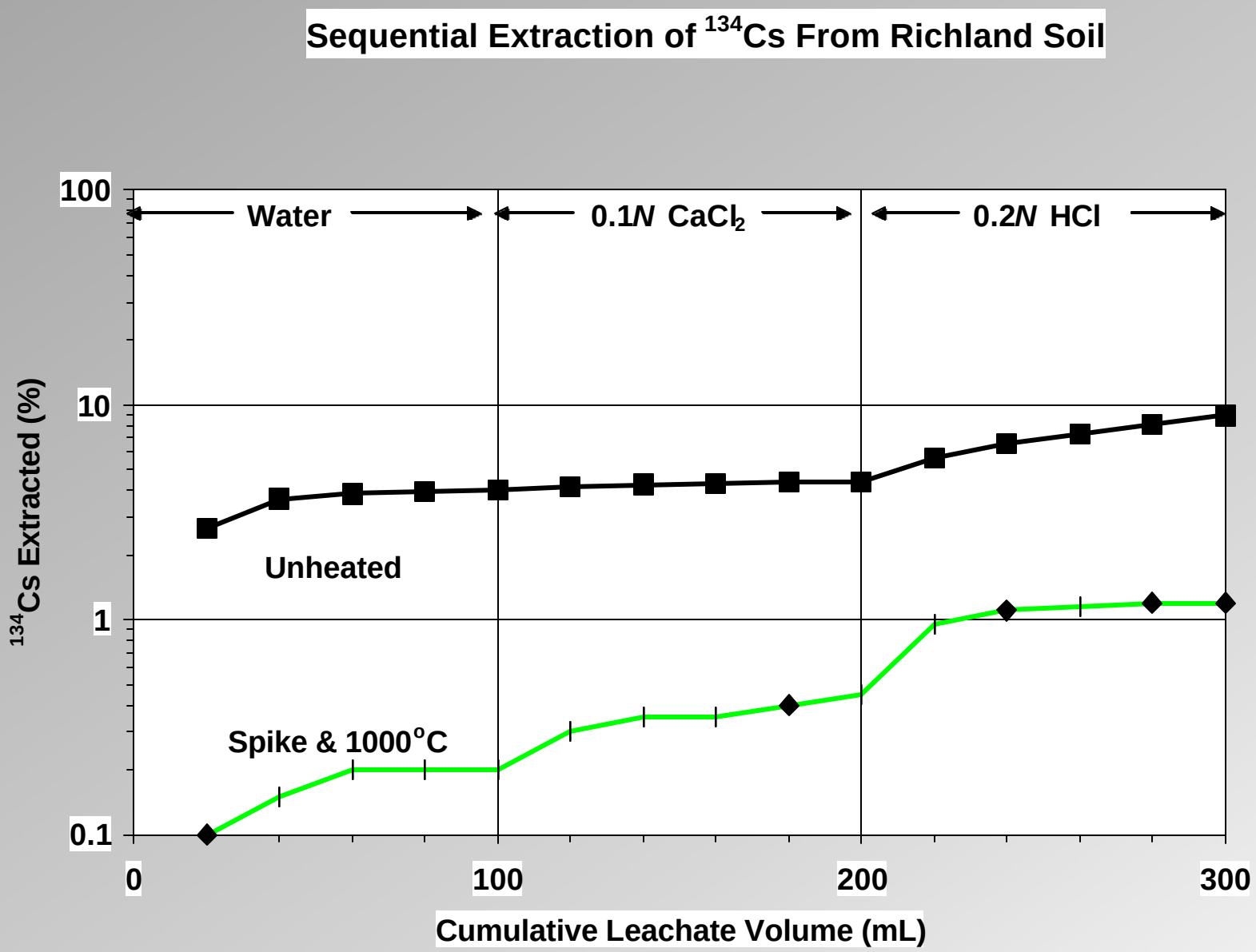


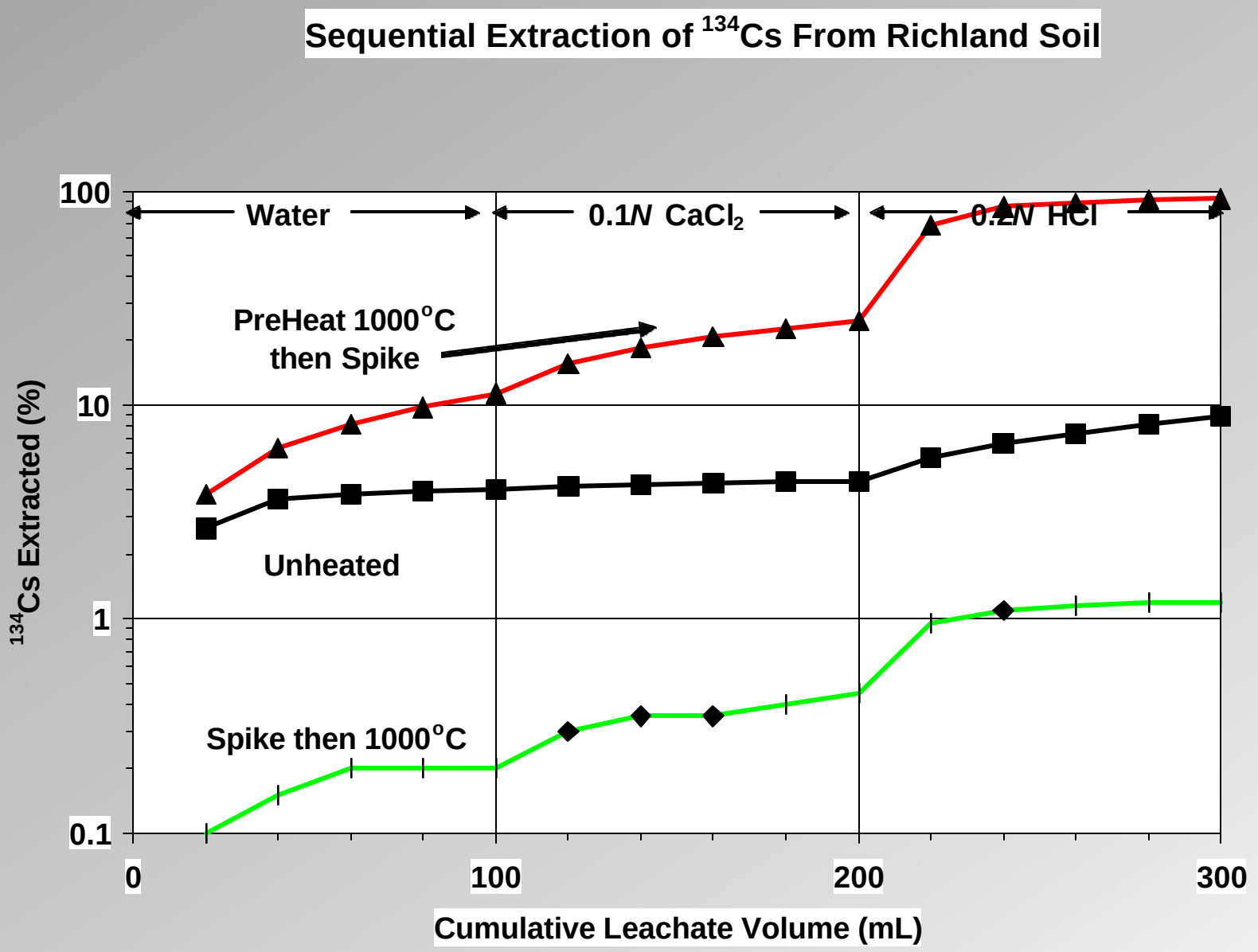

XRD of 57Co-Spiked Heated Quartz
Normalized Intensities with 10% Vertical Offsets
3
2.5
2
1.5
1
0.5
0
10
20
30
40
50
60
70
80
Angle (2q)
1400°C
1200°C
1000°C
800°C
600°C
400°C
200°C
60°C
No Heat

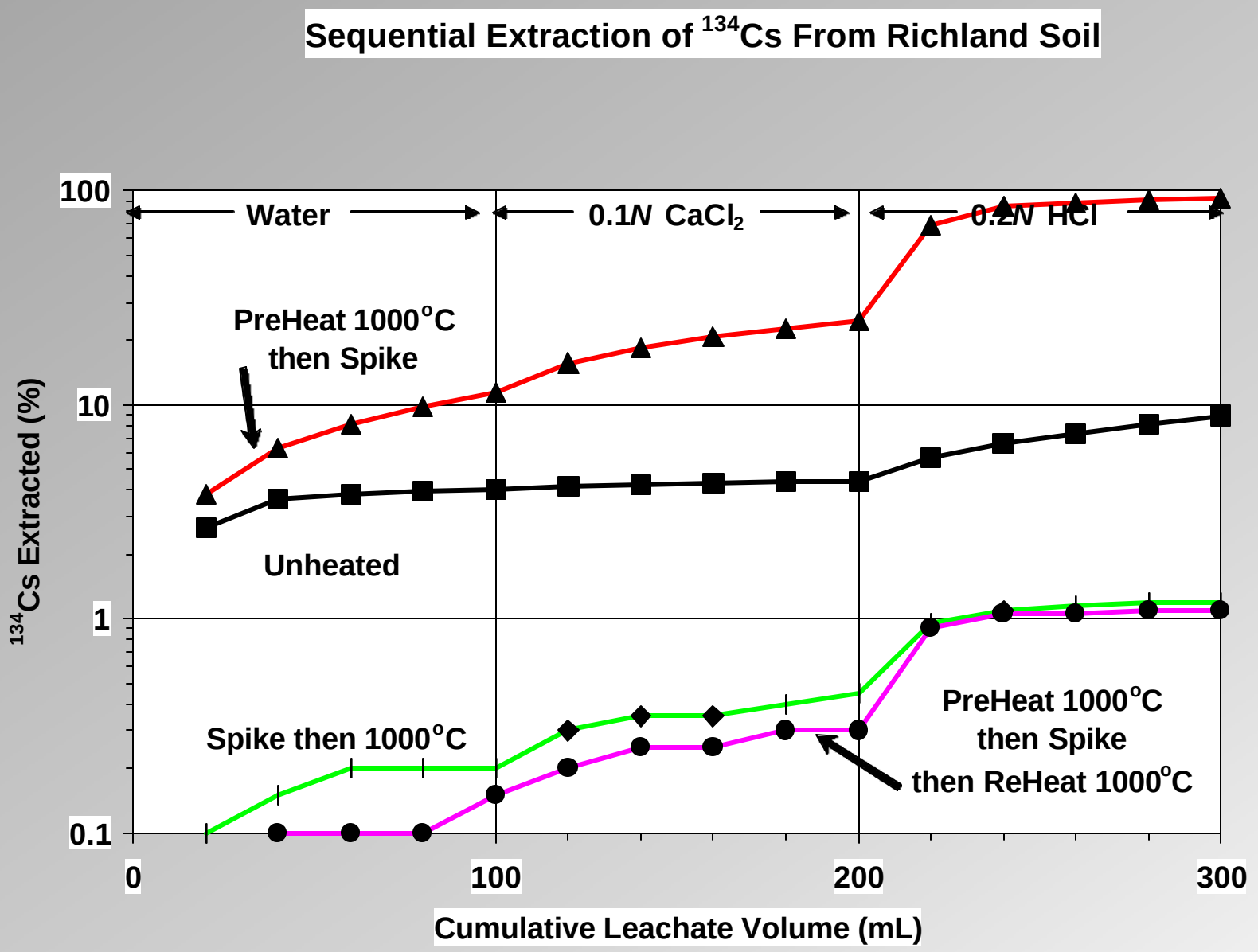

Sequential Extraction of 85Sr From Ottawa Sand (Quartz)
Fraction of 85Sr Extracted
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
100
200
300
Cummulative Extract Volume (mL)
25°C
200°C
400°C
600°C
800°C
1000°C
1200°C
1400°C

Effects of Heating on Soils & Minerals

- Dehydrate minerals, mostly irreversibly (e.g., $2Al(OH)_3$? Al_2O_3)
- Combust organic matter to CO_2 & H_2O
- Metamorphoses of minerals, many irreversibly (e.g., a- ? ß-quartz @ 573°C and clay minerals ? mullite @ 1000°C)
- Decarbonate calcite (e.g., $CaCO_3$? $Ca(OH)_2 + CO_2$ @ 800°C)
- Oxidize reduced species (e.g., $Fe^{2+} + O_2$? Fe^{3+})
- Vitrify (melt) partially or completely
- Sinter mineral particles
- Volatilize some contaminants (e.g., Hg, NO_3^-, ^3H)
- Diffuse ions into minerals
- Open new and/or alter porosity
- Change surface area and its wetability
- Etcetera


Sequential Extraction of ^{134}Cs From Richland Soil
Water
0.1*N* $CaCl_2$
0.2*N* HCl
100
10
1
0.1
^{134}Cs Extracted (%)
Unheated
Spike & 1000°C
0
100
200
300
Cumulative Leachate Volume (mL)


Sequential Extraction of ^{134}Cs From Richland Soil
Water
0.1*N* $CaCl_2$
0.2*N* HCl
PreHeat 1000°C
then Spike
Unheated
Spike then 1000°C
100
10
1
0.1
0
100
200
300
^{134}Cs Extracted (%)
Cumulative Leachate Volume (mL)


Sequential Extraction of ^{134}Cs From Richland Soil
Water
0.1*N* $CaCl_2$
0.2*N* HCl
PreHeat 1000°C then Spike
Unheated
Spike then 1000°C
PreHeat 1000°C then Spike then ReHeat 1000°C
^{134}Cs Extracted (%)
100
10
1
0.1
0
100
200
300
Cumulative Leachate Volume (mL)

Effects of Heating on Soil Minerals

- Dehydrate minerals, mostly irreversibly (e.g., $2Al(OH)_3$? Al_2O_3)
- Combust organic matter to CO_2 & H_2O
- Metamorphoses of minerals, many irreversibly (e.g., a- ? ß-quartz @ 573°C and clay minerals ? mullite @ 1000°C)
- Decarbonate calcite (e.g., $CaCO_3$? $Ca(OH)_2$ + CO_2 @ 800°C)
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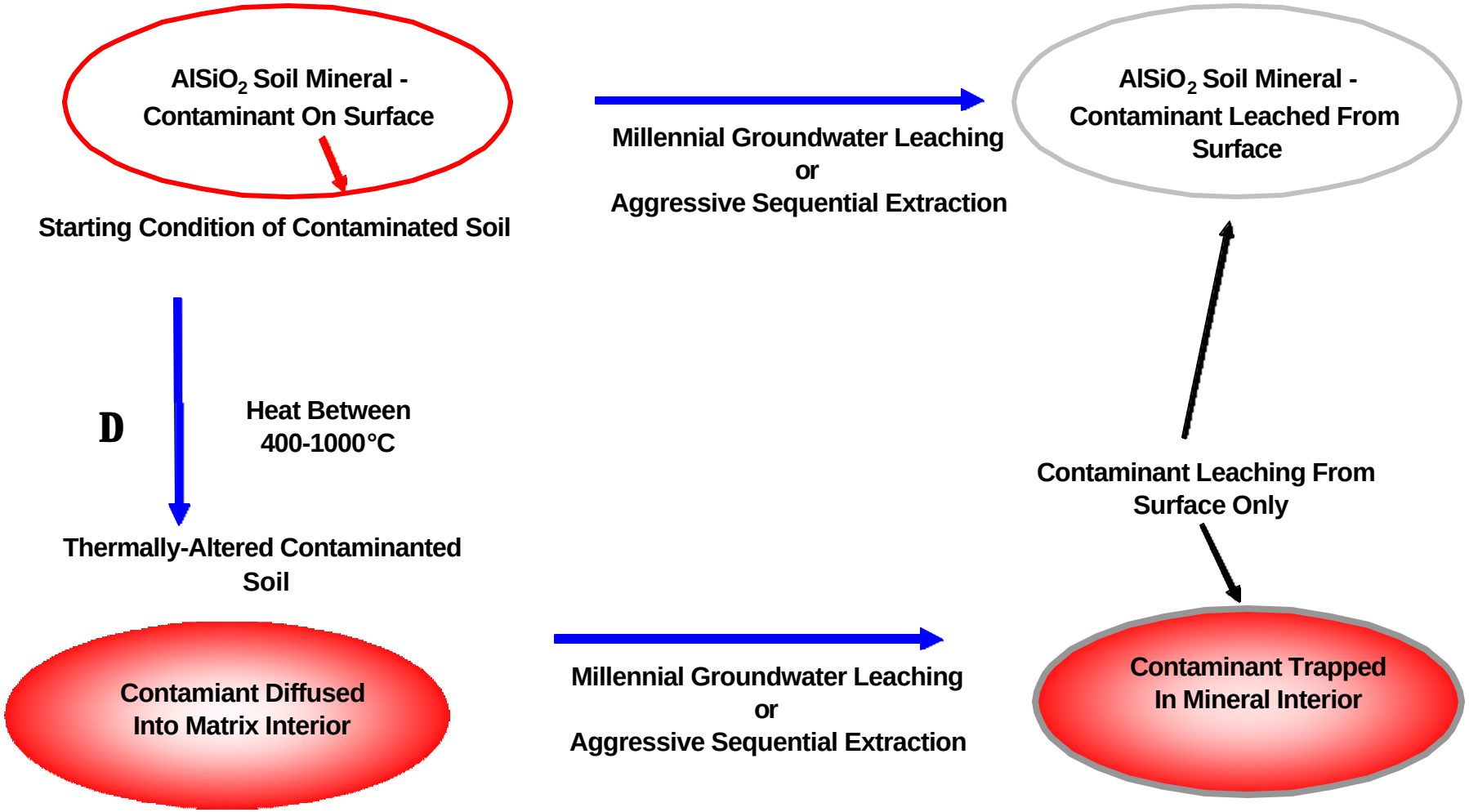
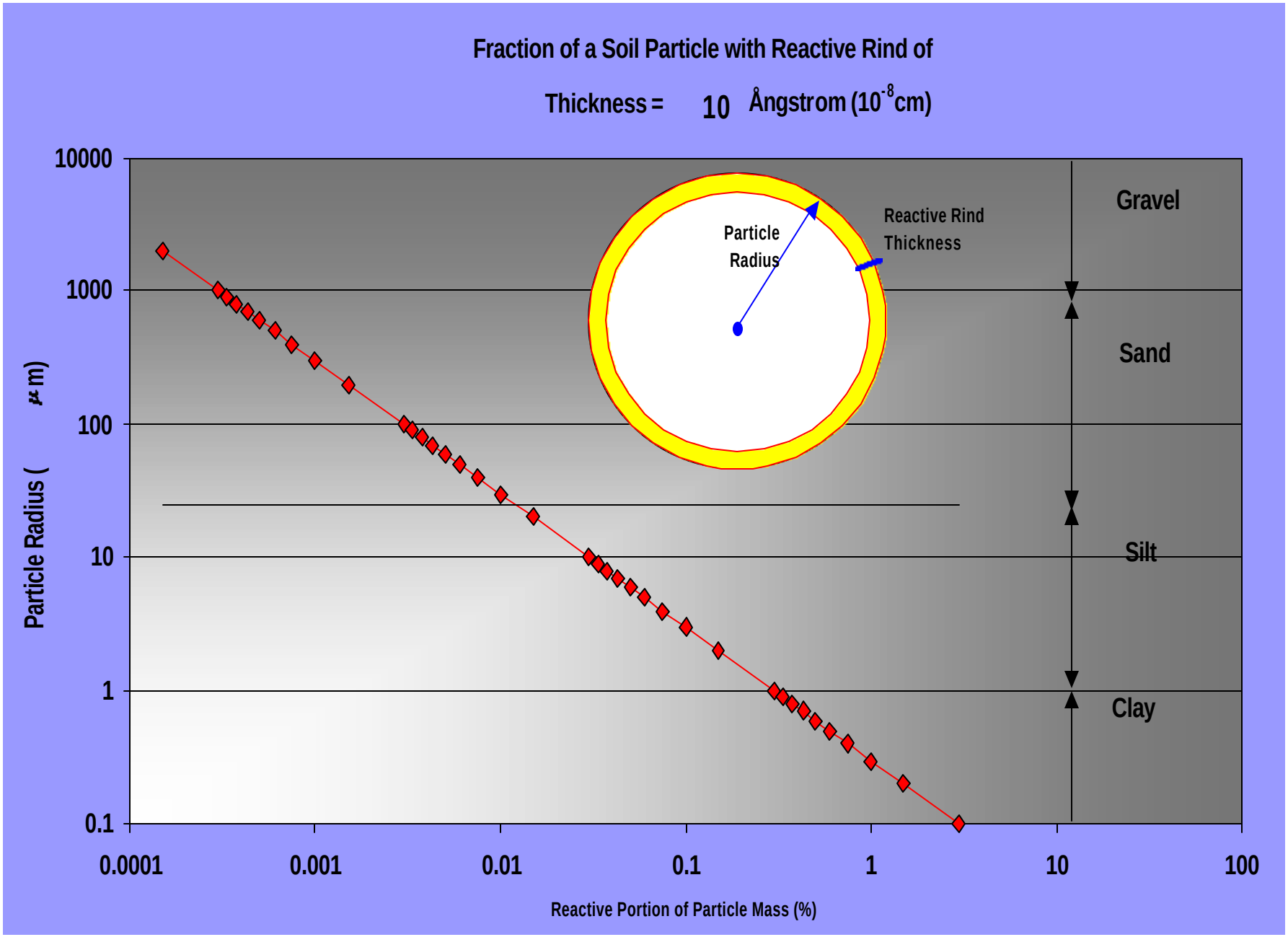
- Sinter mineral particles
- Volatilize some contaminants (e.g., Hg, NO_3^-, ^3H)
- Diffuse ions into minerals
- Open new and/or alter porosity
- Change surface area and its wetability
- Etcetera

Mechanistic Concept For Fixation of Radionuclides In Soil Minerals By Heating



Unused Contaminant Storage Space in All Contaminated Soils!



Diffusion Equations for Modeling Contaminant Temperature Response

Tracer Diffusion Equation for Semi-Infinite Solid, initially with no internal contamination but a contaminant on its surface:

$$c = \frac{Q}{\sqrt{p \cdot D \cdot t}} \exp\left(-\frac{x^2}{4 \cdot D \cdot t}\right)$$

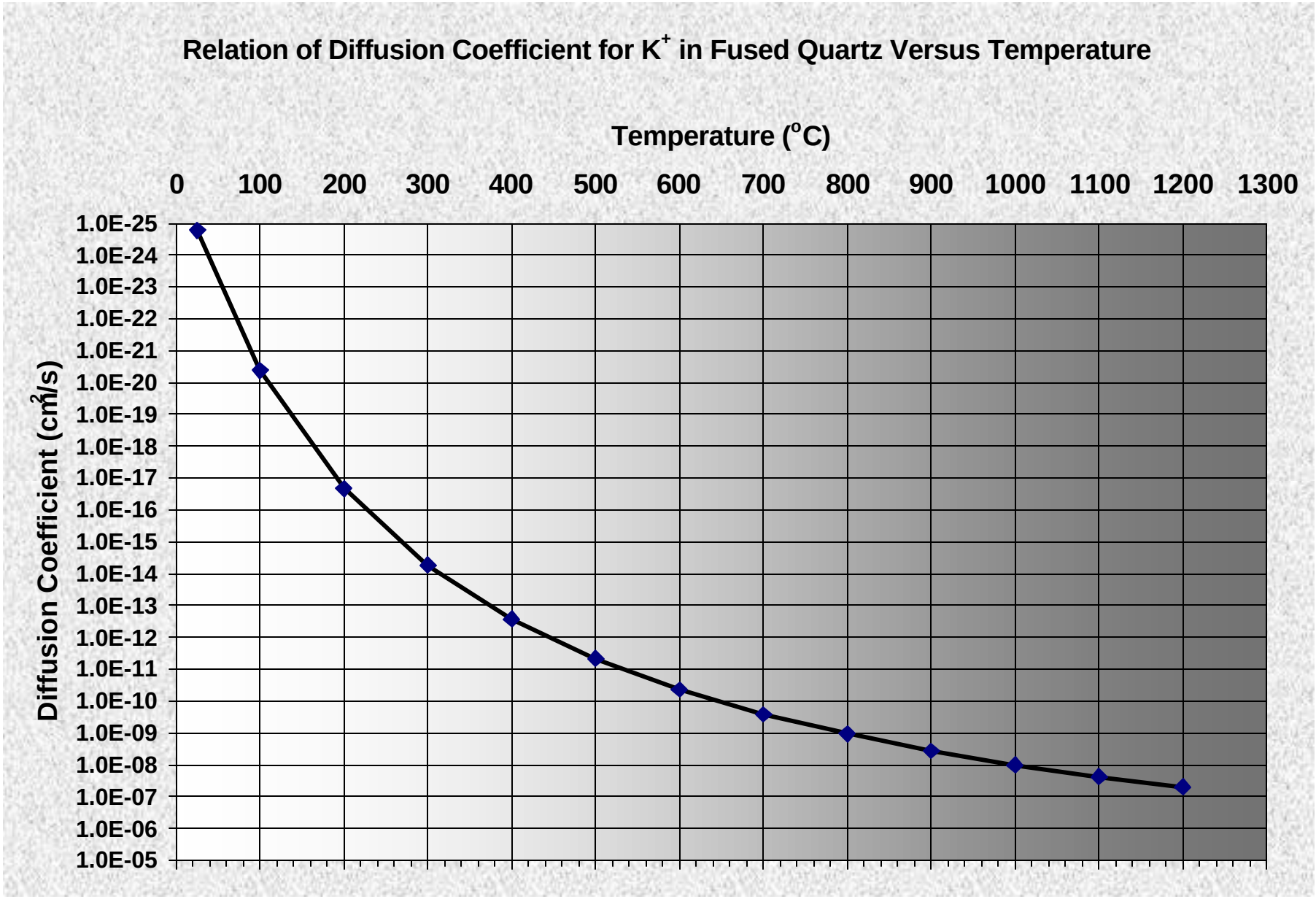
Where,

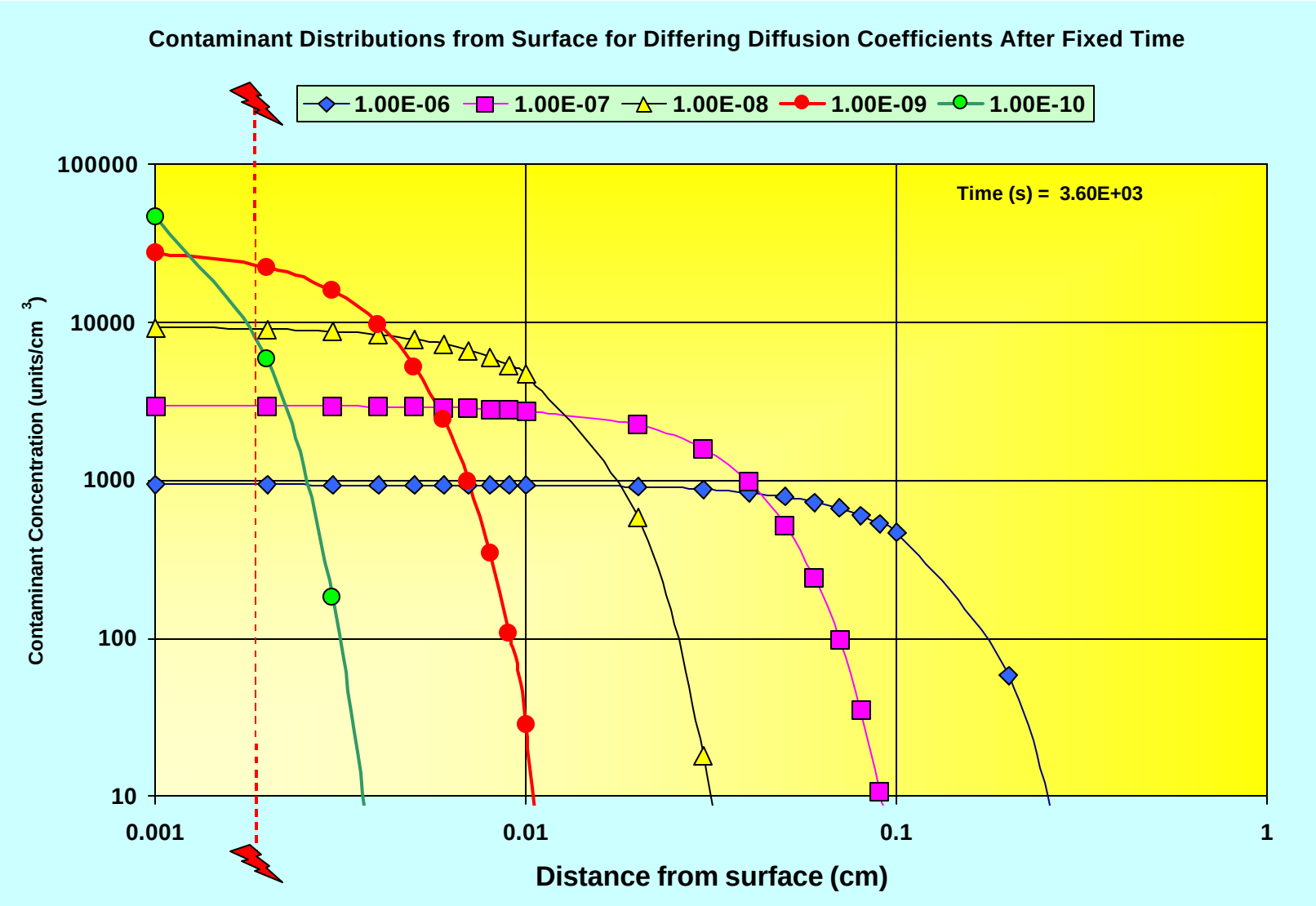
c = contaminant concentration (units/cm^3)
Q = initial contaminant on surface at time-zero (units/cm^2)
D = diffusion coefficient (cm^2/s)
x = distance from surface (cm)
t = time for diffusion (s)

At a given temperature (T), D is approximated by:

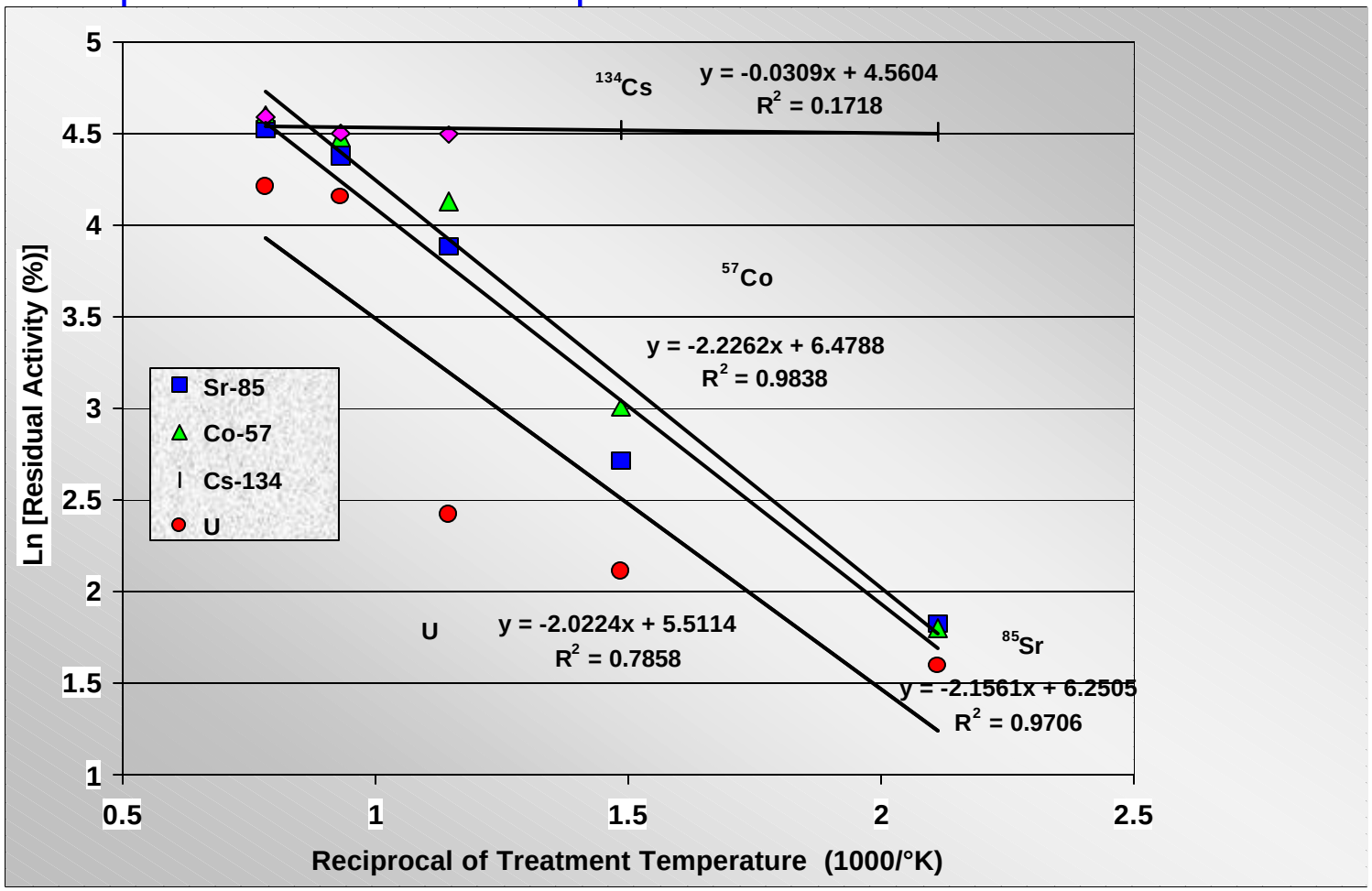
$$D = D_0 \cdot \exp\left(-\frac{E_D}{R \cdot T}\right)$$

Where,
D_0 = pre-exponential factor (e.g., 1.35 x 10^{-3} cm^2/s)
E_D = activation energy (e.g., 125 kJ mole^{-1})
R = universal gas constant (0.008314 kJ °K^{-1}
T = temperature (°K)


Relation of Diffusion Coefficient for K+ in Fused Quartz Versus Temperature
Temperature (oC)
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
Diffusion Coefficient (cm2/s)
1.0E-25
1.0E-24
1.0E-23
1.0E-22
1.0E-21
1.0E-20
1.0E-19
1.0E-18
1.0E-17
1.0E-16
1.0E-15
1.0E-14
1.0E-13
1.0E-12
1.0E-11
1.0E-10
1.0E-09
1.0E-08
1.0E-07
1.0E-06
1.0E-05


Contaminant Distributions from Surface for Differing Diffusion Coefficients After Fixed Time
1.00E-06
1.00E-07
1.00E-08
1.00E-09
1.00E-10
Time (s) = 3.60E+03
100000
10000
1000
100
10
0.001
0.01
0.1
1
Contaminant Concentration (units/cm 3)
Distance from surface (cm)

Residual activity retained after extraction versus log of reciprocal of treatment temperature for Hanford sand



$$D = D_0 \cdot \exp\left(-\frac{E_D}{R \cdot T}\right)$$

Equivalent Heating Times To Attain the Same Degree of Radionuclide Immobilization as 1 hour at 1000°C

Temperature (°C)	Time (hours)	Diffusion Coefficient (cm^2/sec)
1000	1.0	1.00×10^{-8}
900	2.7	3.65×10^{-9}
800	9.0	1.11×10^{-9}
700	38.1	2.62×10^{-10}
600	9 days	4.46×10^{-11}
500	86 days	4.81×10^{-12}
400	4 years	2.67×10^{-13}
300	211 years	5.42×10^{-15}
200	5400 years	2.11×10^{-17}
100	2.7×10^{8} years	4.20×10^{-21}
25	6.91×10^{12} years	1.65×10^{-25}

Summary of Radionuclides Immobilized in Soil Minerals By Thermal Treatment

- **Amount of immobilization increases in each extractive form (residual and acid soluble) with increasing temperature.**
- **Observed for five key DOE contaminant radionuclide tracers (^{85}Sr, ^{134}Cs, ^{57}Co, ^{95m}Tc, and U).**
- **Observed with three common minerals (quartz, feldspar, and calcite) and two soils (Hanford sand and Melton Valley silt).**
- **Amount of immobilization follows an Arrhenius-type relation with temperature**
- **Previous heating does not affect subsequent immobilization with additional heating**
- **Detailed report now published online in *Environmental Science & Technology 2001, 35, 4327-4333.***
- **Need to develop both basic research information and technology development**

Need For Proposed Basic R&D Studies

– ***Get the Contaminant Pictures To Convince Skeptics!***

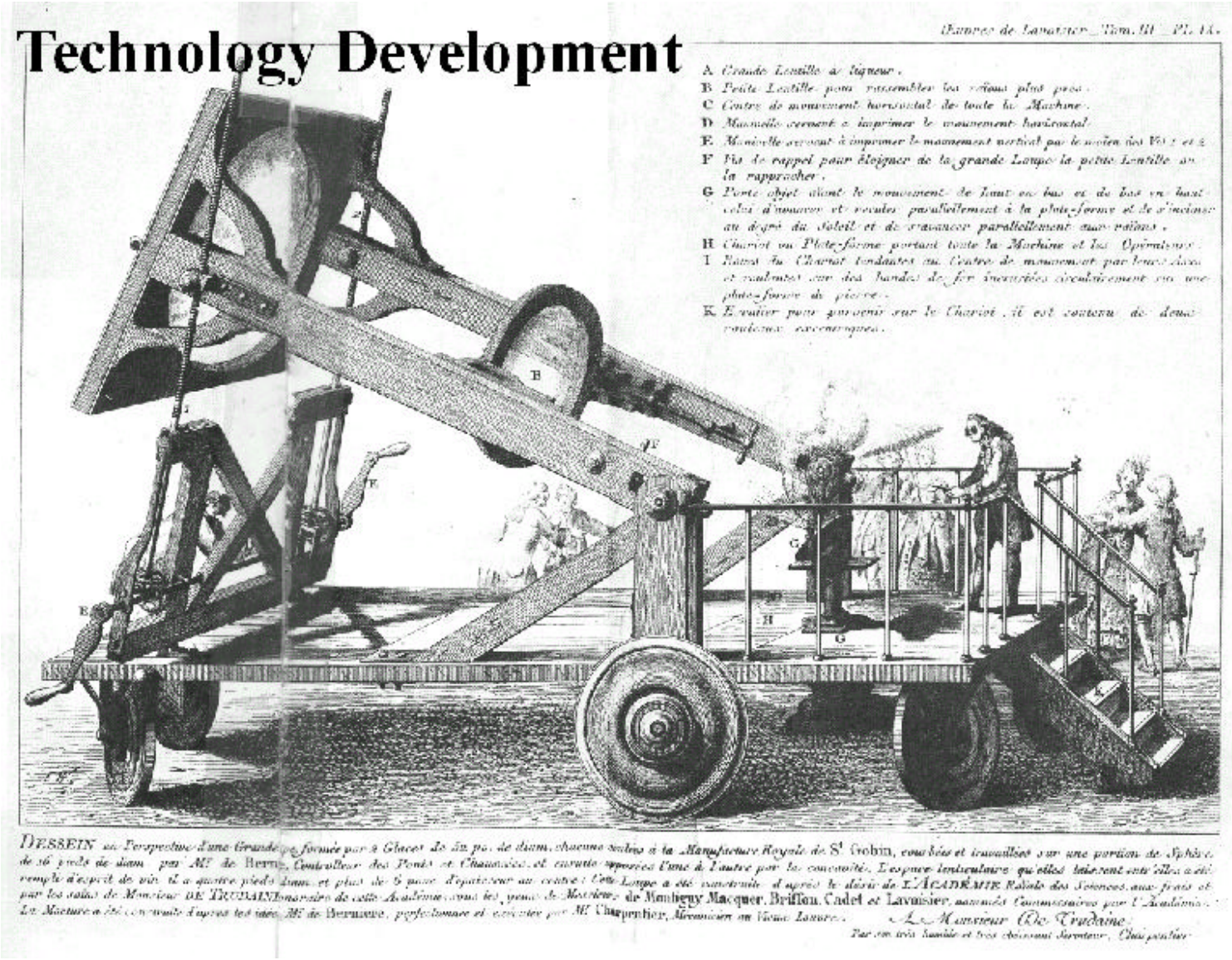
- Autoradiography of α- and β- emitters – ^{89}Sr, ^{99}Tc, and ^{232}U into large (1-cm sized) inert minerals – quartz, corundum, feldspar, mica.
- Energy-Dispersive X-Ray Spectroscopic (EDXS) Images – key stable elemental contaminants (Sr, U, Cr, Cd, and/or Pb)
- Electron Microprobe Analyses (EMPA) Profiles

— ***Nail Down the Diffusion Mechanism To Enable Soil Remediation Performance Assessment!***

- Buying into a thermal treatment diffusion mechanism means buying into a diffusion leaching mechanism too!
- Performance of thermally-altered soil could, thus, be focused on an entirely rational and objective basis.

Stone Soup

Technology Development



Potential Applications For Soil Thermal Fixation

- Ex situ treatment of metal and/or radionuclide contaminated soil (e.g., rotary kiln)
- In situ treatment of any non-volatile metal and/or radionuclide contaminated soil source or primary plume with convective and/or conductive heat transfer
- In situ co-treatment of volatile and nonvolatile contaminants (e.g., tritium & strontium-90 or TCE & uranium) with off-gas collection

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Fig. A.7. Quadrant 3, bottom, looking southeast.

Scenario For Remediation Technology Development

Strictly on empirical basis:

- Select problem site soils (like tank 1A residual soil) and test for leaching of contaminants after heating to various temperatures
- Address field contaminated soil source configuration.
- Identify in situ soil heating technique(s).
- Develop soil off-gas containment, processing, and monitoring technique.
- Develop soil temperature and configuration monitoring technique.
- Measure “before” and “after” groundwater contaminant concentration and flux effects.
- Measure “before” versus “after” altered soil leaching characteristics.

Important Questions To Compare Environmental Technologies

- How much will it cost?
- Will it work? Oh really, even in Oak Ridge?
- How much more will it cost if we actually use it?
- How many rolls of duct tape does the technology require?

In Situ Techniques For Possible Use in Soil Thermal Treatment

- Inserted vertical electric resistive heaters (e.g., Terratherm www.terratherm.com)
- Hot Gas Injection – Air/steam or combustion gas similar to thermally-enhanced soil vapor extraction
- In Situ Vitrification – www.geomelt.com
- Plasma torch - www.vanguardresearch.com/peps/technical/plasma%20torch.htm
- Burning Glass (Antoine Lavoisier 1777)
- Dielectric Heating (RF/Microwave) – can generate heat in situ – www.macrowave.com/rftech.html
- Induction – www.ameritherm.com

Stone Soup – Current Status

- Heat samples of Tank 1A residual soil and sequentially extract – ^{90}Sr, ^{137}Cs, Transuranics (Am, Pu, Cm, Th) and Uranium Behavior
- Question has changed from “Why should we heat soil?” to “How can we heat soil?”
- Identify in situ heating techniques and compare with all remedial alternatives.
- This presentation is available www.ornl.gov\LANGMUIR\StoneSoup.pdf