# Long-term Permeability and Reactivity of Granular Iron: Effects of Gas Formation and Mineral Precipitation

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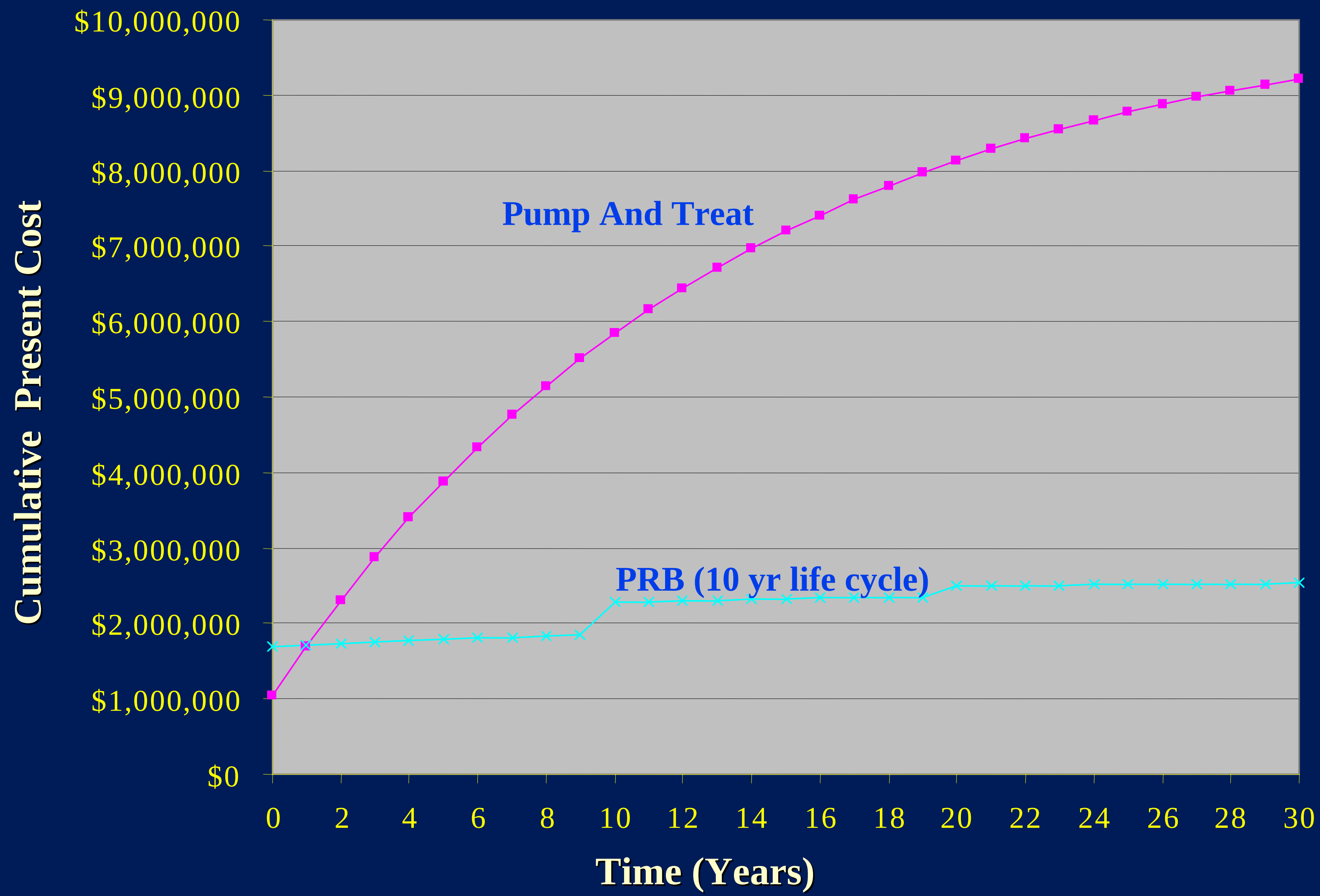
# Cost Comparison




Vidumsky, EPA PRB short course

# Economic Benefit Requires Low O&M Costs

- **Requiring "Long-Term" maintenance-free performance of the granular iron**

1. Longevity of the iron
2. Continued reactivity
3. Permeability

Precipitation formation

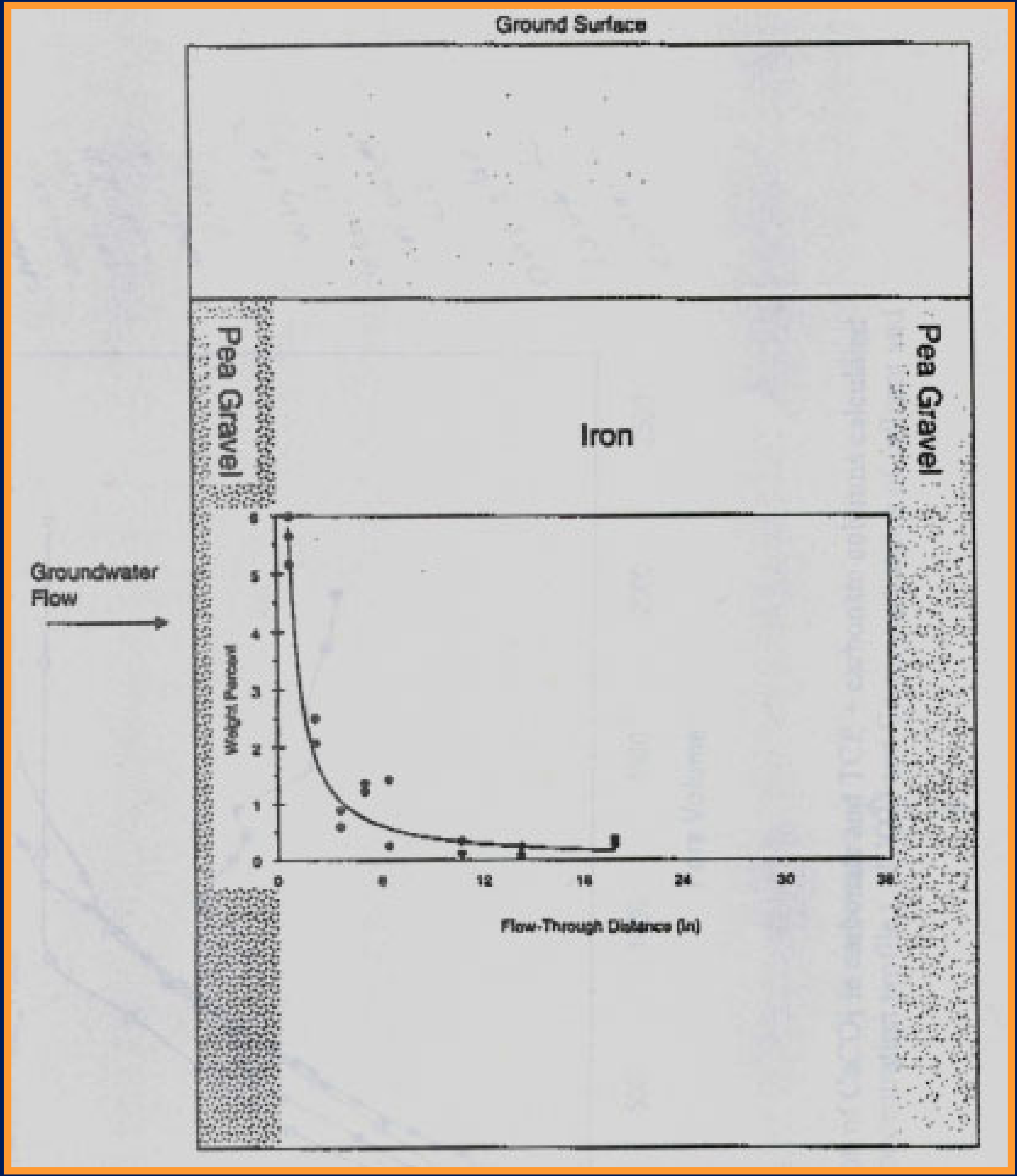
# Gas Formation and Precipitation of Carbonate Minerals

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^-$$

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$$

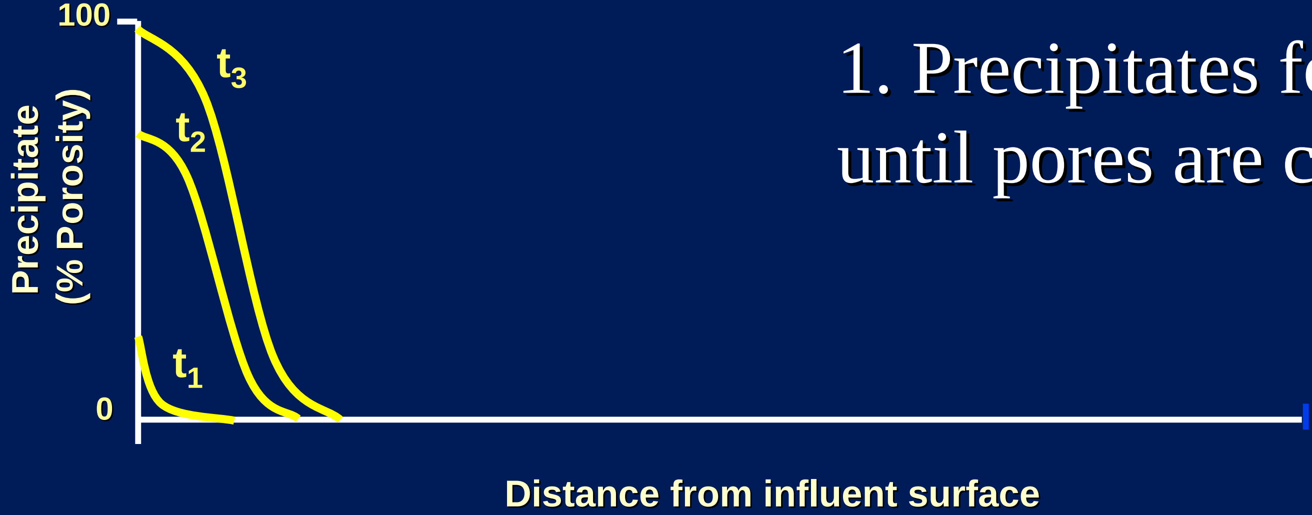
$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3\downarrow$$

Precipitate formation commonly observed in laboratory studies and at field sites

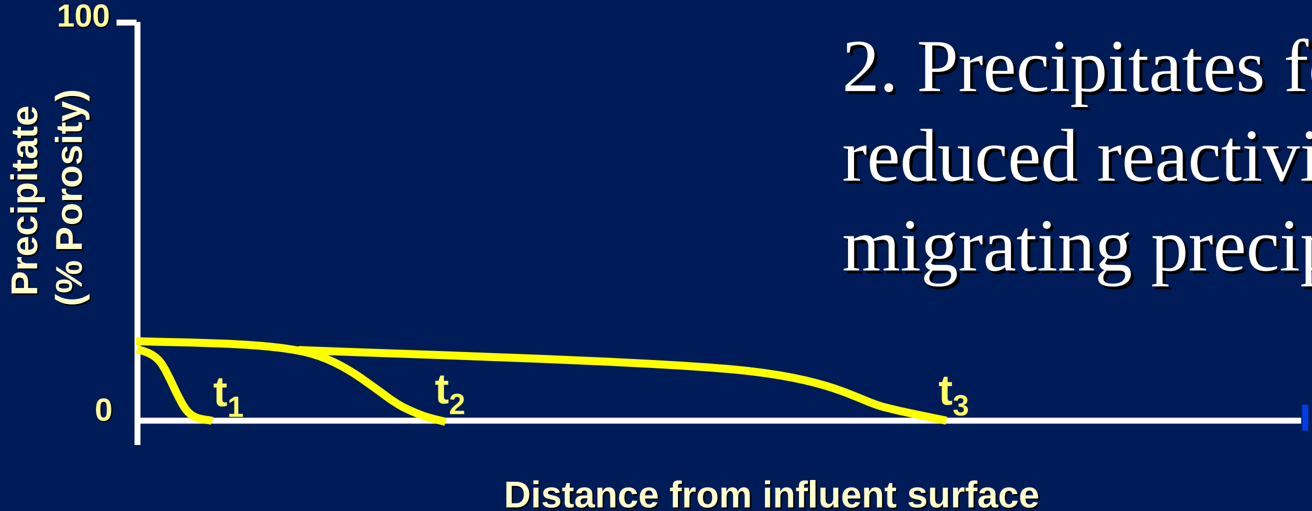



A field site, NY (Vogan et al., 1999. J. Hazard. Mat. 68, 97-108.)

# Consider two possibilities




1. Precipitates form at inlet until pores are clogged (IRB)




2. Precipitates form causing reduced reactivity → migrating precipitate front

- **Most current models for predicting precipitate formation use the iron corrosion rate to “drive” the reaction and assume the rate to be constant**

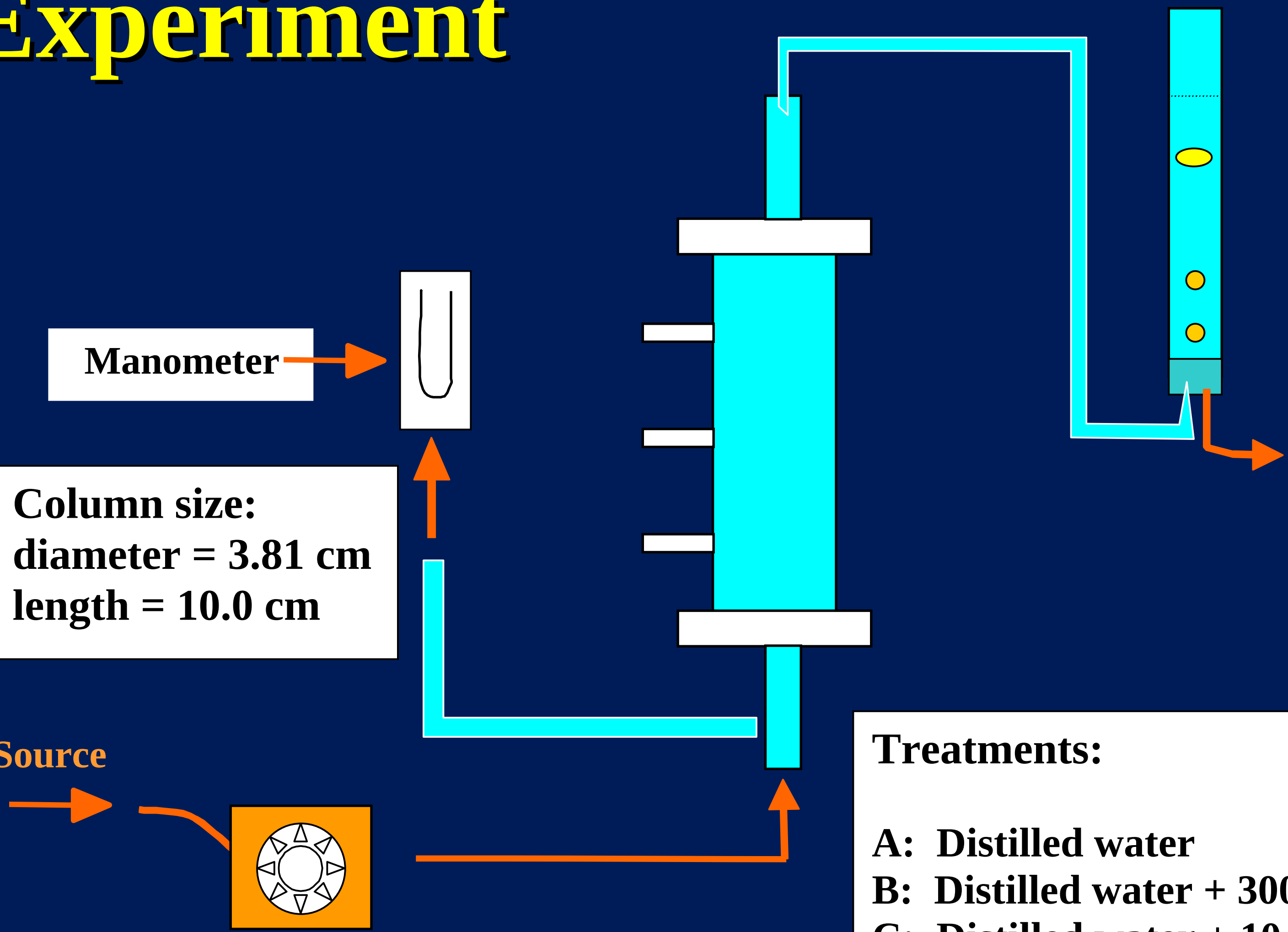
- **This leads to predictions of impermeable reactive barrier (IRB) formation**

# Objectives

- Study the effects of entrapped gas and carbonate minerals on porosity and hydraulic conductivity in granular iron columns

- Examine the effect of precipitates on iron reactivity using TCE as an indicator

# Experiment



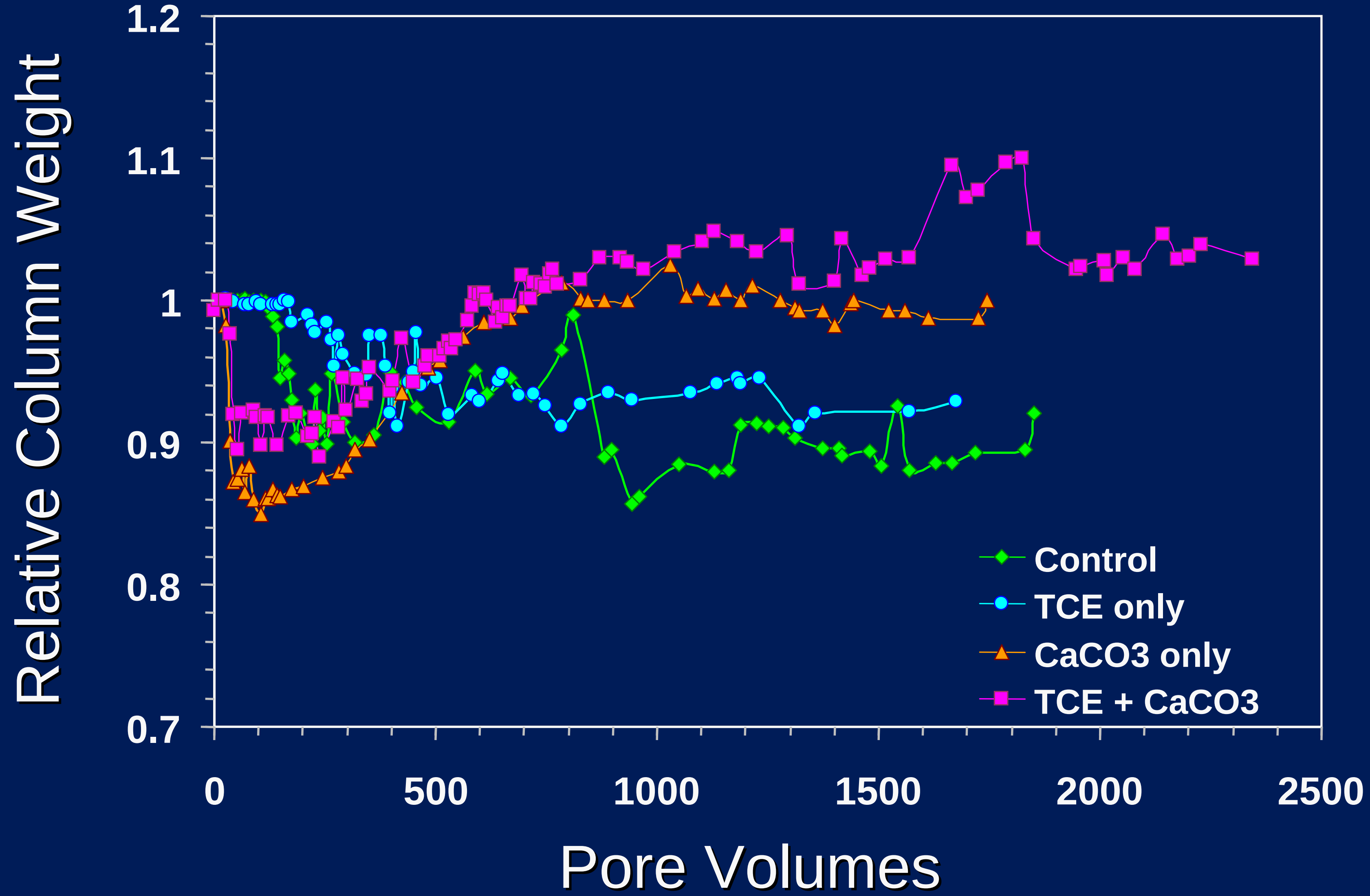

**Column size:**
**diameter = 3.81 cm**
**length = 10.0 cm**

**Treatments:**

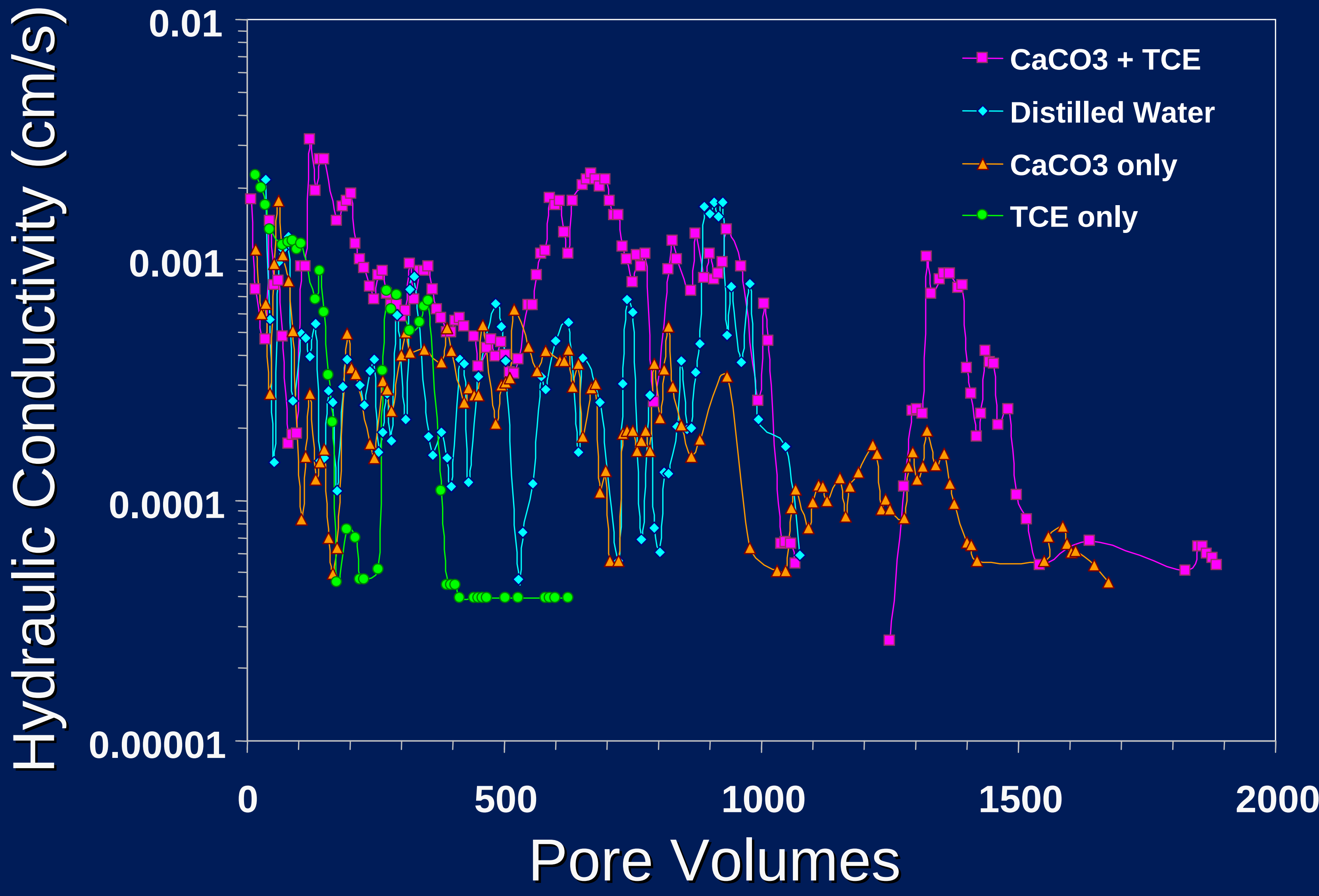
**A: Distilled water**
**B: Distilled water + 300 ppm $CaCO_3$**
**C: Distilled water + 10 ppm TCE**
**D: Distilled water + 10 ppm TCE +3 300 ppm $CaCO_3$**

**Flow rate: 85 cm / day**

# Changes in Column Weight due to Gas Generation and Precipitation



# Effects of $CaCO_3$ on Hydraulic Conductivity

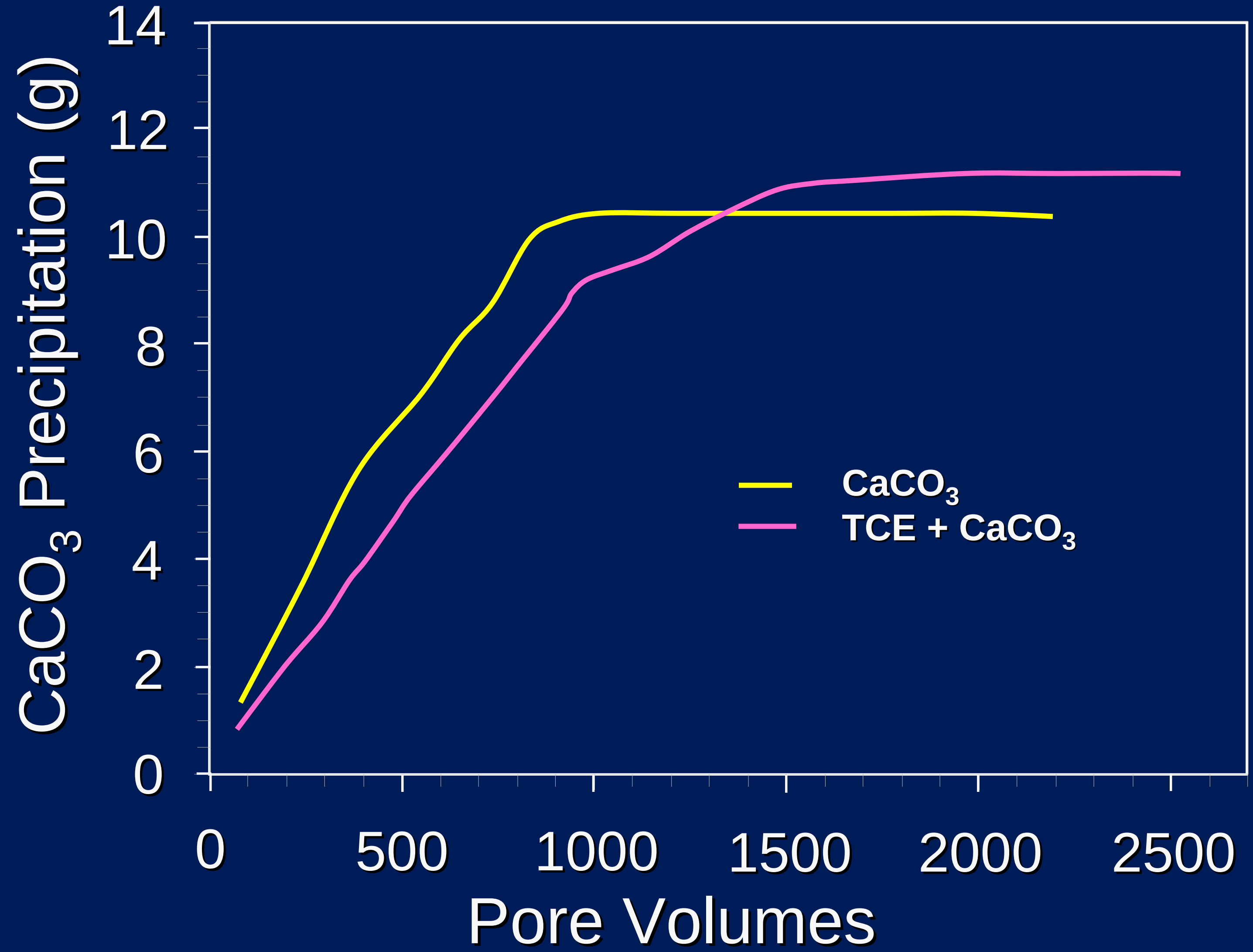


# Changes in Porosity and Hydraulic Conductivity in the Column

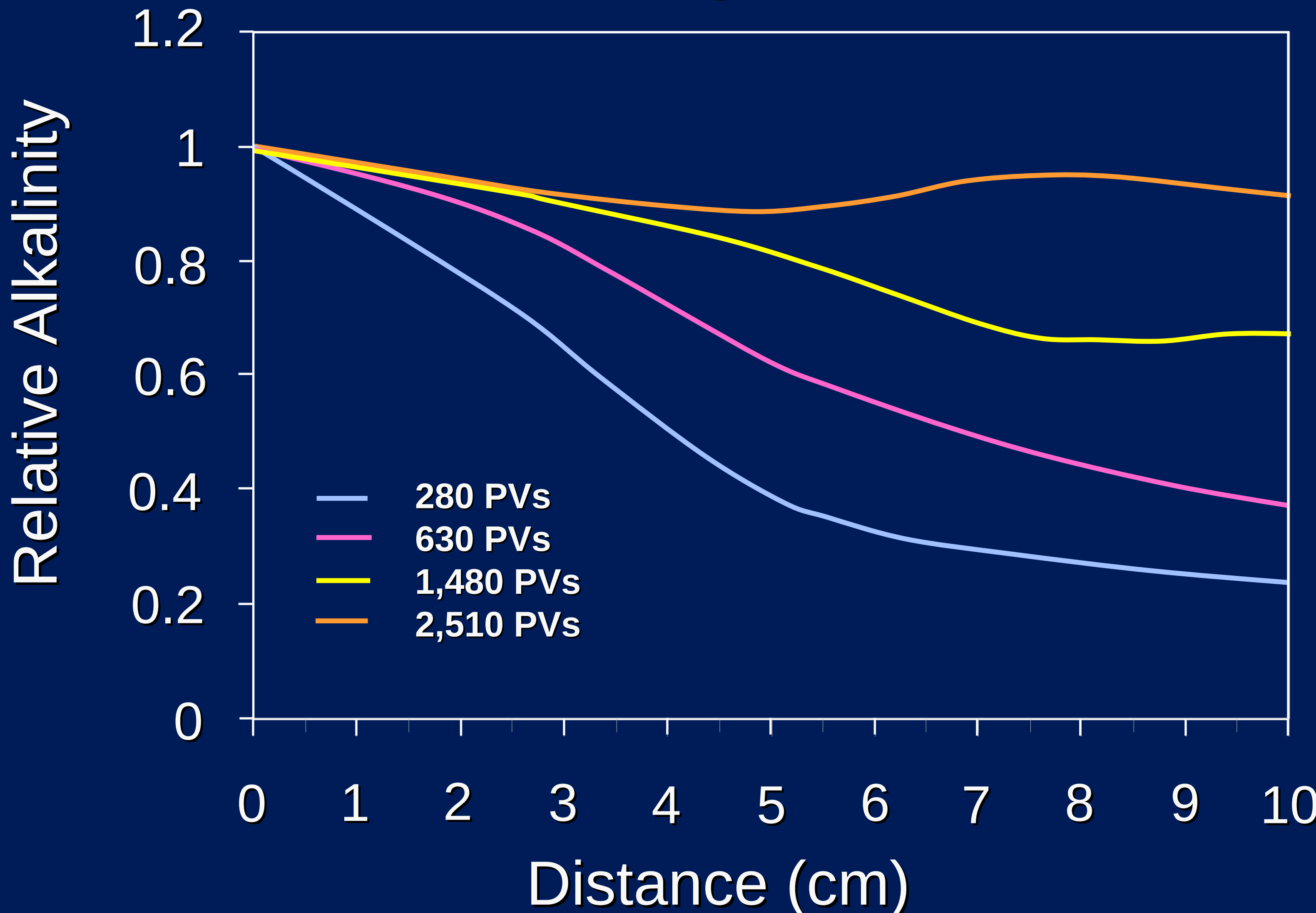
| | Porosity Loss (%) | Hydraulic Conductivity Loss (%) |
|---|---|---|
| Gas | 10 % | 50 – 80 % |
| Precipitates | 7 % | ~ 0 |

- $H_2$ gas — non-wetting, occupies large pores
- precipitates — surface coating, < 0.01 μm

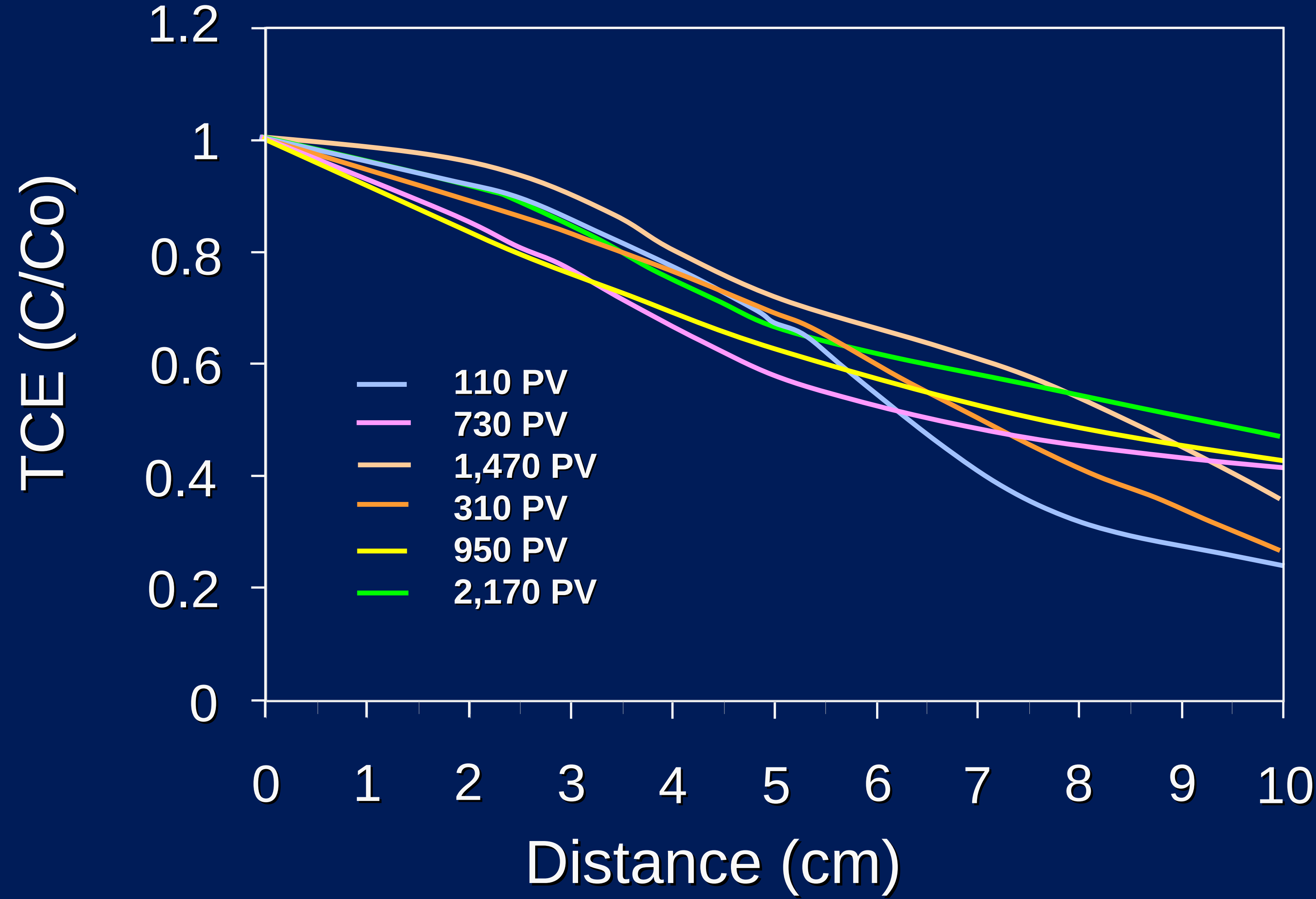
# Carbonate Precipitation in Iron Columns



# Alkalinity Along the Iron Column
## (300 ppm $CaCO_3$ + 10 ppm TCE)



# TCE Profiles Along the Iron Column (10 ppm TCE)



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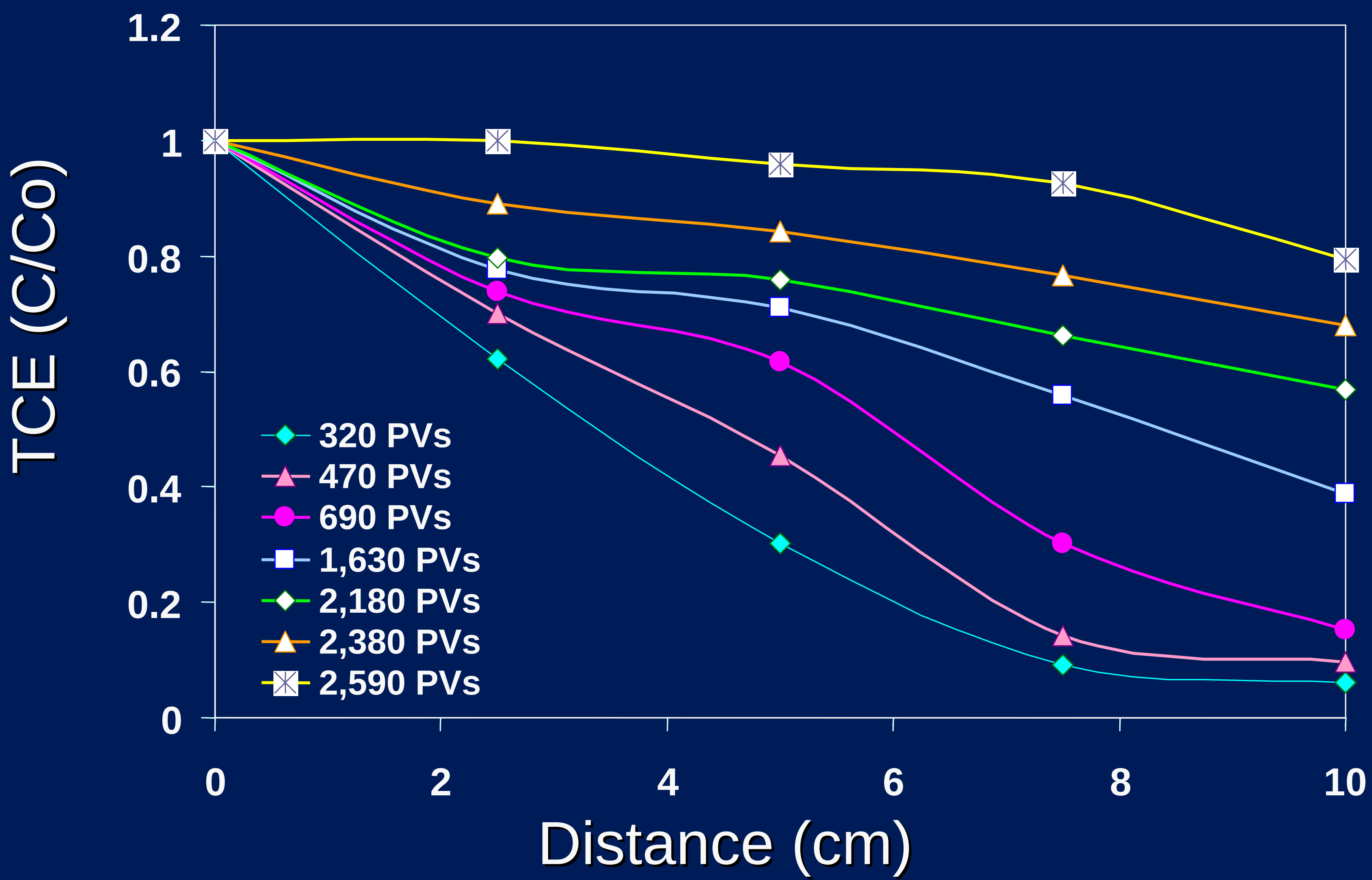
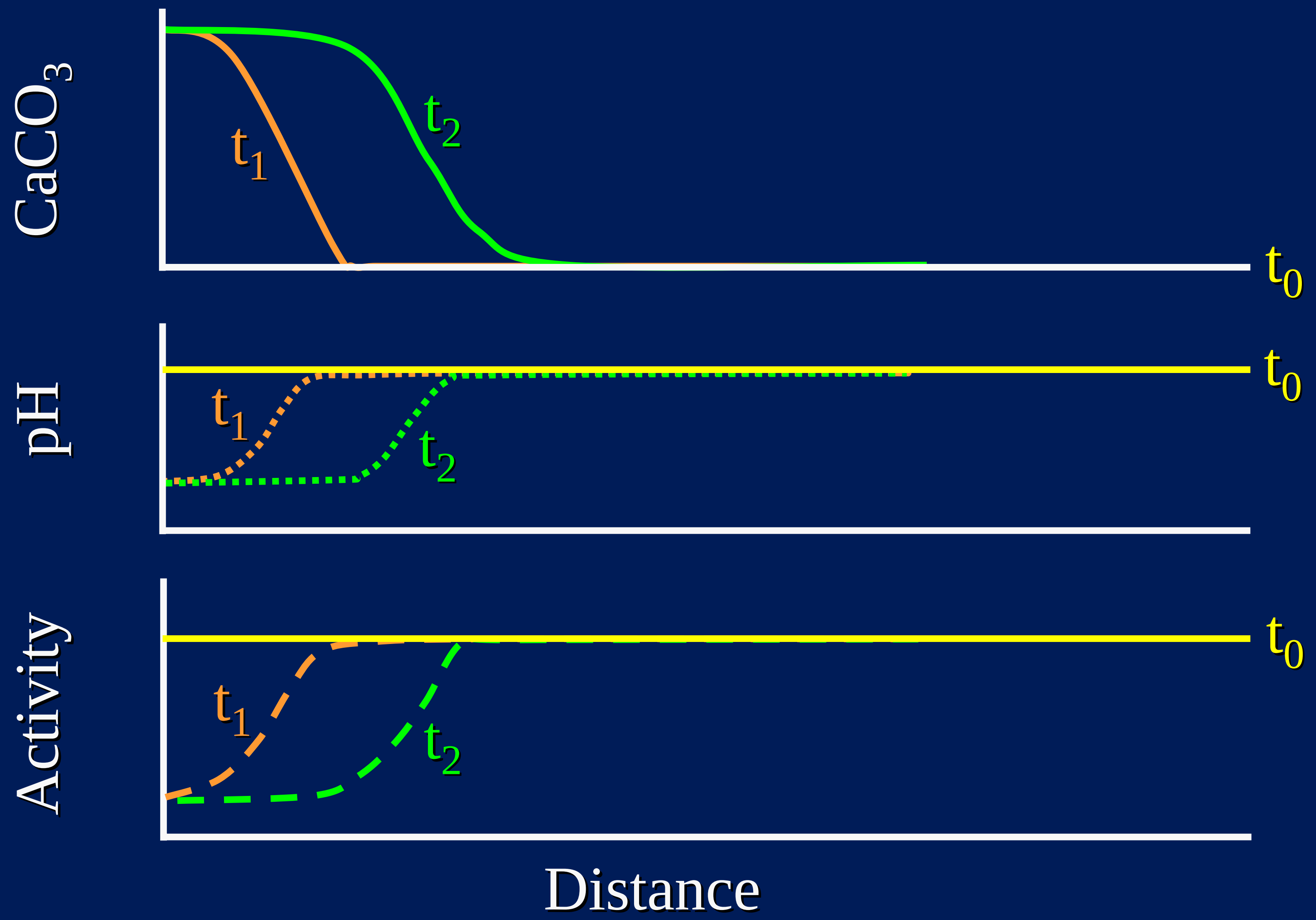


# Conceptual Model



# Implications

$CaCO_3$ accumulates to 0.1 g/cm$^3$ of iron

Assume:

- 100 mg/L decline in $HCO_3^-$
- porosity of geologic formation -- 0.33
- groundwater velocity of 10 cm/day

*Precipitate front will advance at a rate of **1.3 cm/yr***

# Conclusions

1. Entrapped gas causes initial rapid decline in hydraulic conductivity but partially recovers once bubbles are appeared in the effluent
2. Calcium carbonate precipitates occupies up to 7% initial pore spaces in the column
3. Precipitates cause reduction in degradation rates.
4. Calcium carbonate precipitates form as a progressing front as a consequence of reduced iron activity

# Conclusions (cont'd)

5. Precipitates do not cause a significant decline in hydraulic conductivity
6. Under field conditions calcium carbonate precipitate front will progress very slowly
7. Based on our current understanding the rate of precipitate formation may be predictable and has the potential to be incorporated in design

# Acknowledgement

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