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Morning Speaker August 1

Reuse of Water Plant Residuals as Deicing Chemicals

REUSE OF WATER PLANT RESIDUALS AS DEICING CHEMICALS

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OUTLINE

- Chloride deicing salts, use and impacts
- Organic deicers – use and impacts
- Water plant residuals
- Deicers from water plant residuals
- Freezing point depression and ice melting studies
- Conclusions

Chloride salts as deicers

Chloride deicers commonly used: NaCl, $CaCl_2$, $MgCl_2$

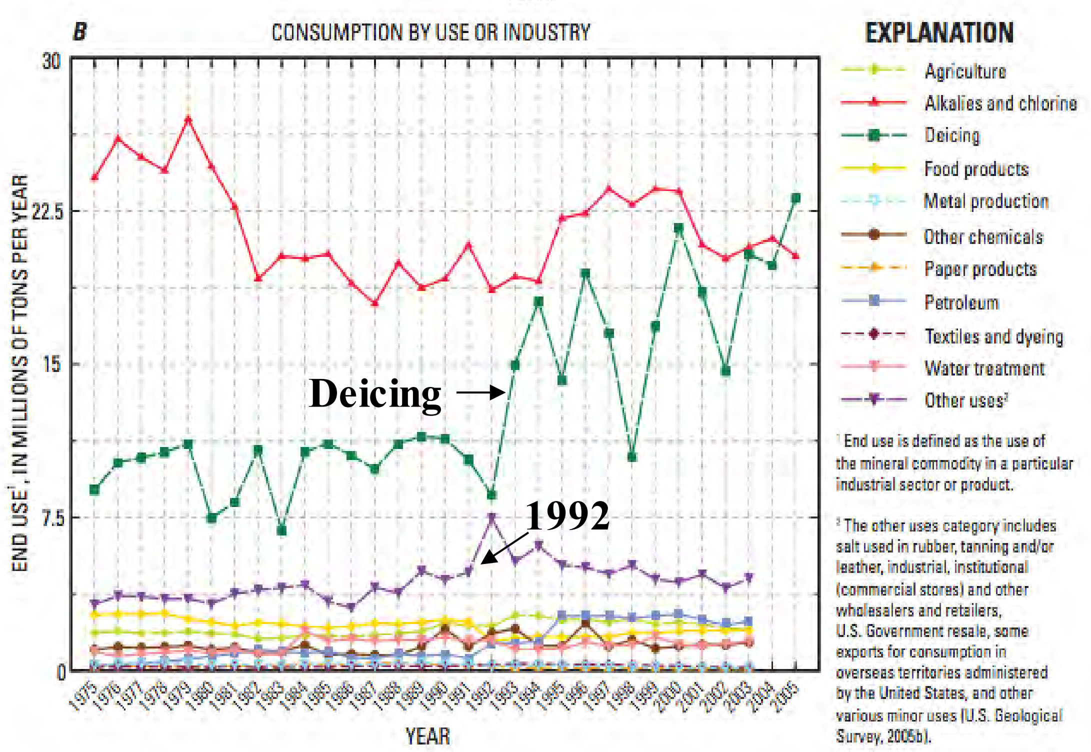


Figure 1. Salt use and consumption in the United States by *(A)* all end users, 1975–2003 (data from U.S. Geological Survey, 2005b), and *(B)* consumption by use or industry, 1975–2005 (data from U.S. Geological Survey, 2005b; Kostick and others, 2007).

Salt consumption by industry

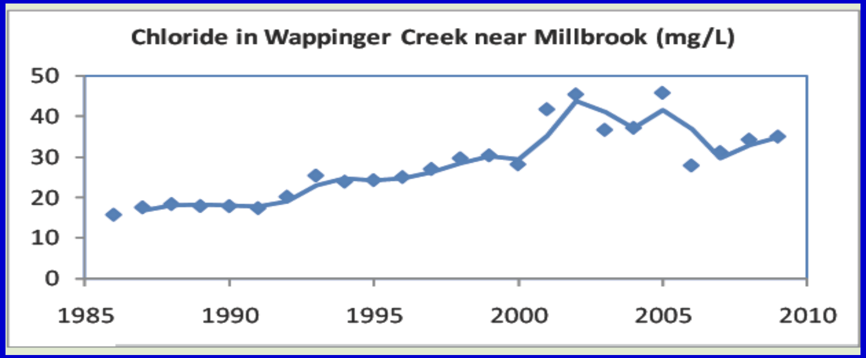
Road salt use Mt/yr

Year	Amount used	P*
1950	0.5	151
2020	22	330

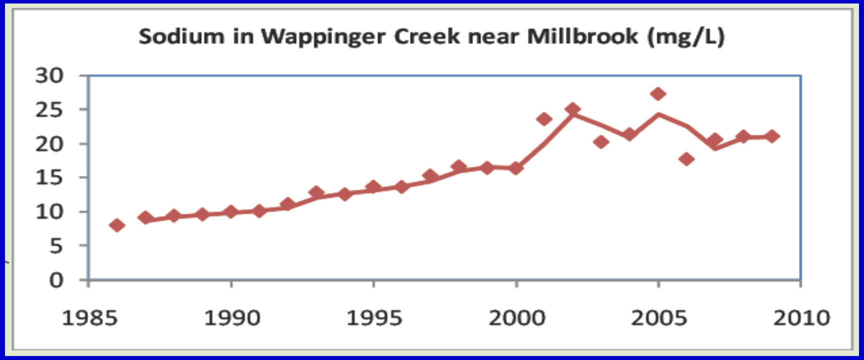
*P: Population (M)

Environmental Impacts Of Road Salt Usage

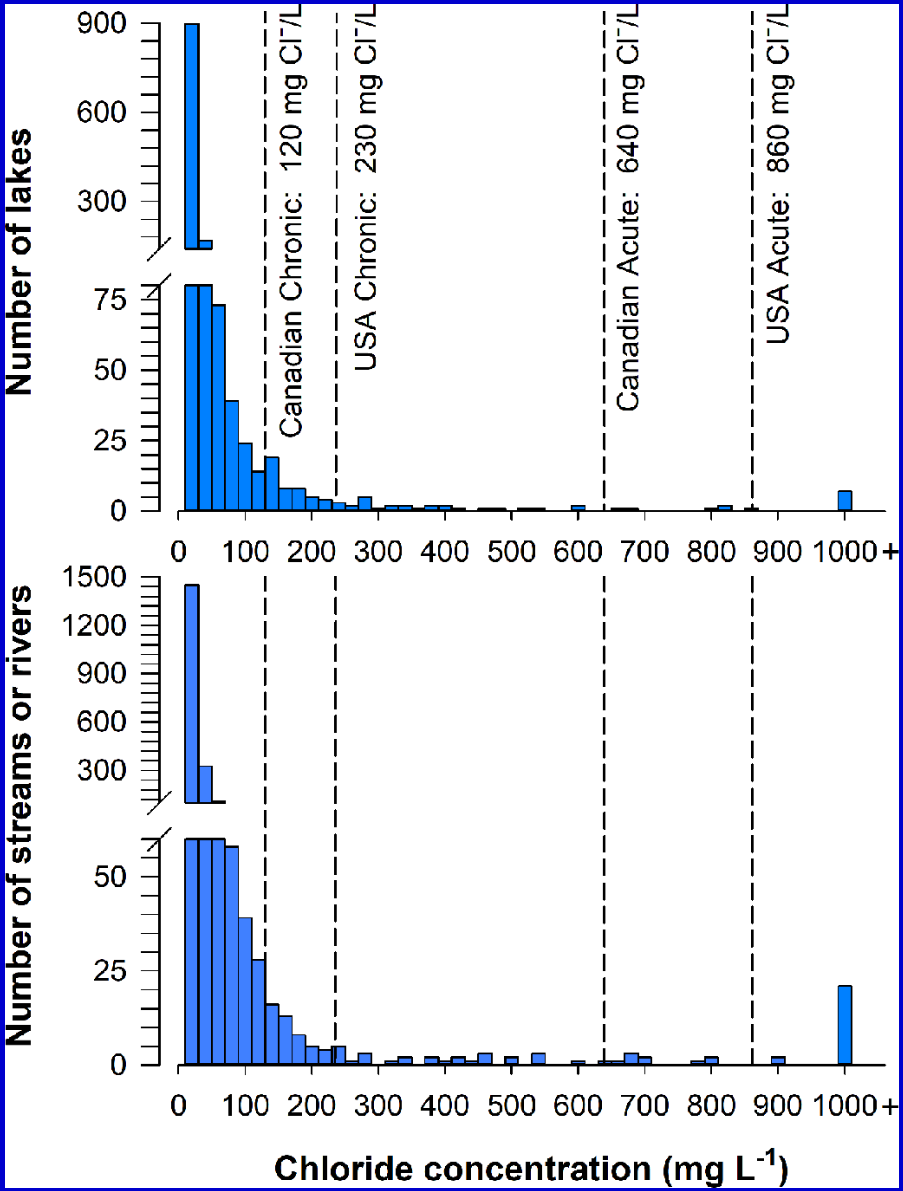
- Groundwater, surface water, and soil contamination, vegetation damage



Chloride increase in stream: Duchess County, NY, Kelly et al, *Environ Sci Technol* **42**: 410–15.



Sodium increase in stream: Duchess County, NY.



EPA (Environmental Protection Agency). 2012. National Aquatic Resource Surveys data. Washington, DC: EPA.

Chloride concentrations in lakes

Chloride concentrations in rivers

Hintz, et al, Road salts, human safety and the rising salinity of waters, Front Ecol Environ 2022.

Kaushal et al, Freshwater salinization syndrome: from emerging global problem to managing risks , Biogeochemistry, 2021.

Corrosion Related Damages from chloride deicers

Accelerated corrosion of automobiles

Damage to bridge decks and pavements

Damage to buildings and parking garages

Damage to underground utilities

Corrosion of concrete and rebar

Damage to vegetation

Transportation problems from snow and ice in winter

Biodegradable deicers as alternatives

- **Biodegradable deicers: acetates and formates**
  CMA, KA, NaA, KF, NaF
- **Advantages:** Acetates and formates degrade to CO_2
  CMA: Ca and Mg improve soil properties
- **Disadvantages: High cost**
  - CMA: **~$2,000/ton;** Road salt: **~$100/ton**
- **Oxygen depletion** in receiving waters

  Use additives to mitigate oxygen depletion

** Deicing agents containing oxygen release compounds, Patent No. 11,384,269, Issue Date: July 12, 2022, Inventor: Alexander P. Mathews*

Goals

Reduce cost of raw materials for CMA synthesis

- **Reuse lime softening** water plant sludge as a source of Ca and Mg
- Acetic acid produced via chemical synthesis is costly with a high carbon footprint
- **Use bioprocess to obtain acetic acid from renewable resources**

**Low pH Process for Fermentation of Sugars from Carbohydrates for the Production of Organic Acids and Biodegradable Deicers, Inventors: A. P. Mathews and S. S. Veeravalli, U.S. Patent 11,186,852 Issue Date: November 30, 2021.*

Water plant residuals

- Coagulation process for **turbidity removal**

  Coagulant sludge: $Al(OH)_3$, or $Fe(OH)_3$

  and clays, oxides, etc from turbidity removed

- **Water softening for hardness removal**

  Water softening sludge: $CaCO_3$, $Mg(OH)_2$,

  plus contain coagulant sludge

Quantities of dry residuals: Coagulation*

Population	Flow (mgd)	Low Mt* /yr	High (Mt/yr)
30,000	4.5	132	593
110,000	16.5	484	2,174
400,000	60	1,760	**7,904**
1,000,000	150	4,400	19,761

****Roth et al., AWWA Journal, 2008***

*Mt – metric tons

Quantities of dry residuals: Water treatment plants with softening*

Population	Flow (mgd)	Low Mt/yr*	High (Mt/yr)
30,000	4.5	1,406	3,466
110,000	16.5	5,155	12,709
400,000	60	18,744	42,955
1,000,000	150	43,555	107,388

*Roth et al., AWWA Journal, 2008

*Mt/yr: Metric tons/yr

Water plant sludge management

- **Regulations**
  - Discharge to receiving waters prohibited
  - Landfills: RCRA regulations
- Management alternatives

  Storage in lagoons, drying, land application

  Mechanical dewatering and land application

  - Mechanical dewatering, calcination, reuse
- Cost of land disposal: **~$30 to $120/ton**

Sustainable management

- Reuse water softening sludge to produce **deicing chemicals**

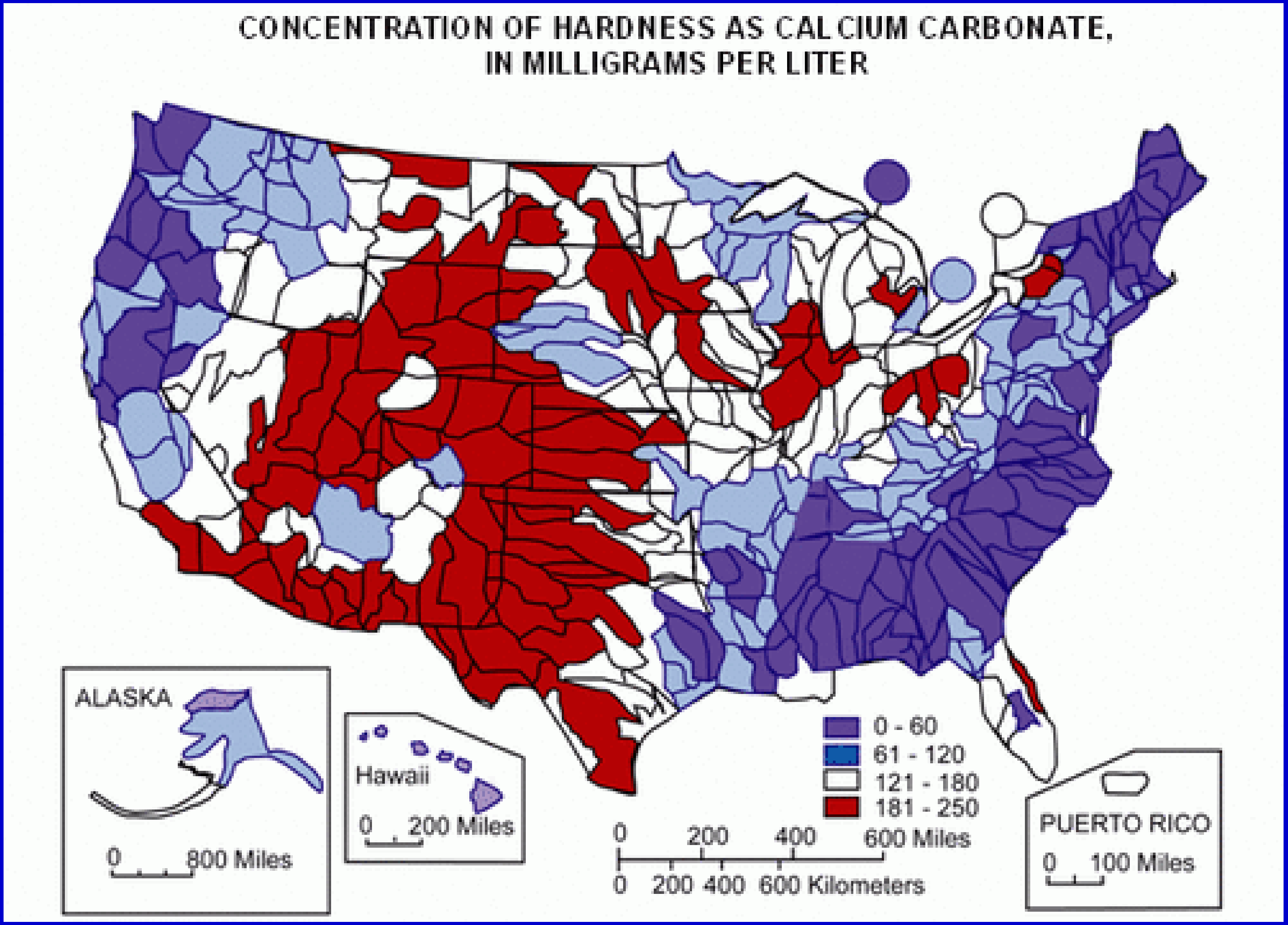
  Calcium magnesium acetate (CMA)

  Calcium magnesium propionate (CMP)

- CMA and CMP are biodegradable and non-corrosive road deicers

Current CMA synthesis

By reacting petroleum-derived acetic acid with Ca and Mg oxides or dolomite



Softening sludge production (U.S.): ~3.1 million tons/yr

Potential CMA production: ~5.2 million tons/yr

Deicer production options

- Water treatment plant with integrated deicer production facility
- Regional deicer production facility

Annual lime sludge production and stockpiles for selected Iowa cities, (van Leeuwen, et al, 2011)

City (Iowa)	Population	Dewatering method	Drying method	Dry weight (tons/yr)	Stockpiled dry weight (tons)
Des Moines	400,000	Filter press	Kiln, air dry	30,700	166,000
Cedar Rapids	128,000	Centrifuge, lagoon	Air dry	16,000	10,500
West Des Moines	52,000	Filter press	Kiln, air dry	3,600	500
Ames	50,000	Lagoon	Air dry	5,170	79,000
Newton	21,000	Lagoon	Kiln, Air dry	3,500	86,000
Boone	17,000	Lagoon	Air dry	3,300	14,700
Indianola	13,000	Lagoon	Air dry	600	6,000
Pella	9,900	Lagoon	Air dry	1,600	9,100
Totals	690,900			64,470	371,800

Studies to evaluate sludge reuse potential

- Evaluate use of water softening sludge for CMA and CMP deicer synthesis
- Compare ice melting rates of synthetic CMA and softening sludge-CMA
- Compare ice penetration depths for synthetic CMA and softening sludge-CMA
- Examine freezing point depression prediction model results

Freezing point depression model

- Activity coefficient γ

$$ln\,\gamma = \frac{-A_1\sqrt{I}}{(1+B\sqrt{I})} + Cm$$

Determine γ of CaA vs concentration

- Osmotic coefficient ϕ

$$\phi = 1 + \frac{A_1}{B^3 I}\left[-\left(1+B\sqrt{I}\right) + 2\,ln\left(1+B\sqrt{I}\right) + 1/\left(1+B\sqrt{I}\right)\right] + \frac{1}{2Cm}$$

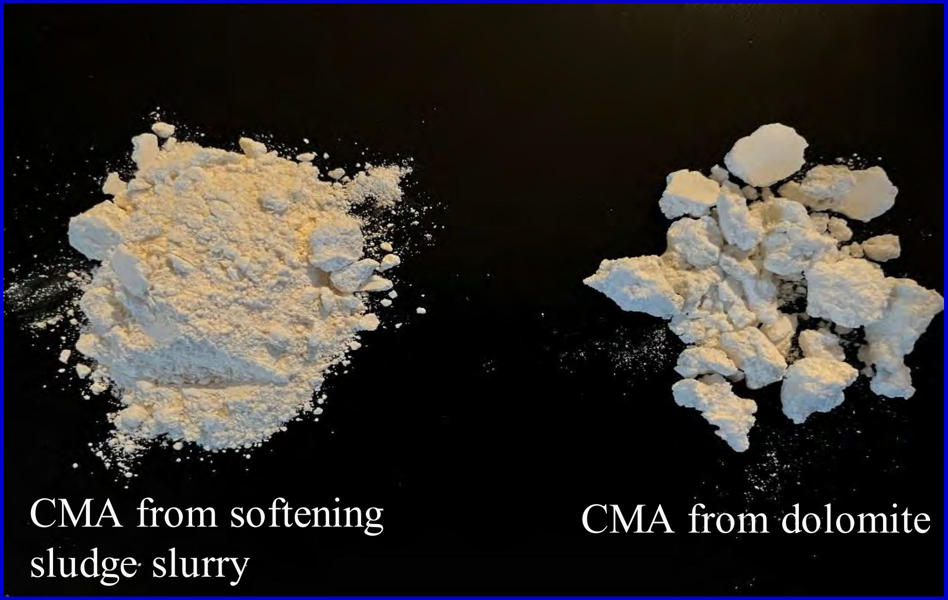
- Freezing point depression θ

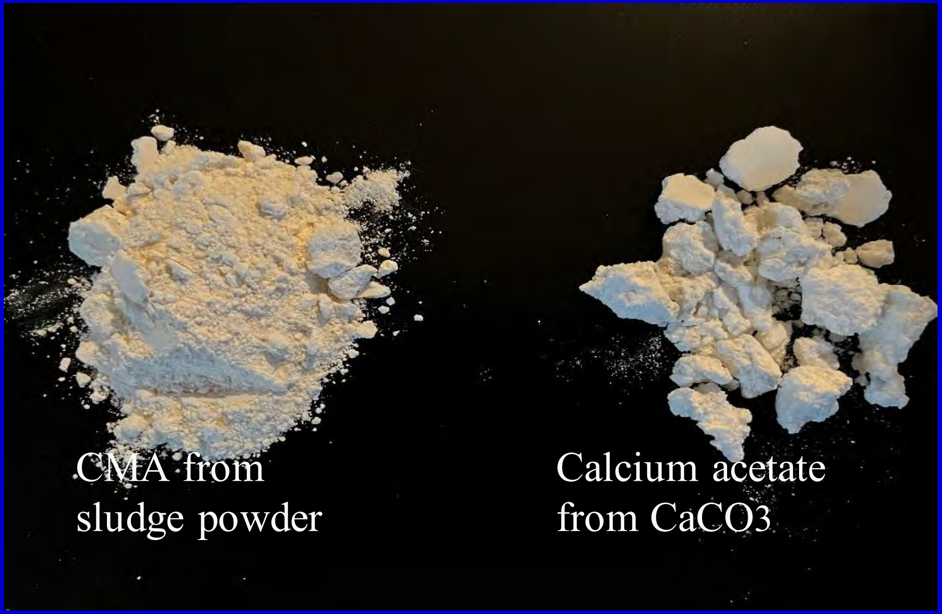
$$\theta = \phi(\lambda_0 + \lambda_1\phi + \lambda_2\theta^2 + \lambda_3\theta^3)\nu m$$

Mathews, Effectiveness of water softening residuals as components of road deicing chemicals: Model analysis of freezing point depression, Journal of Environmental Management, 2021

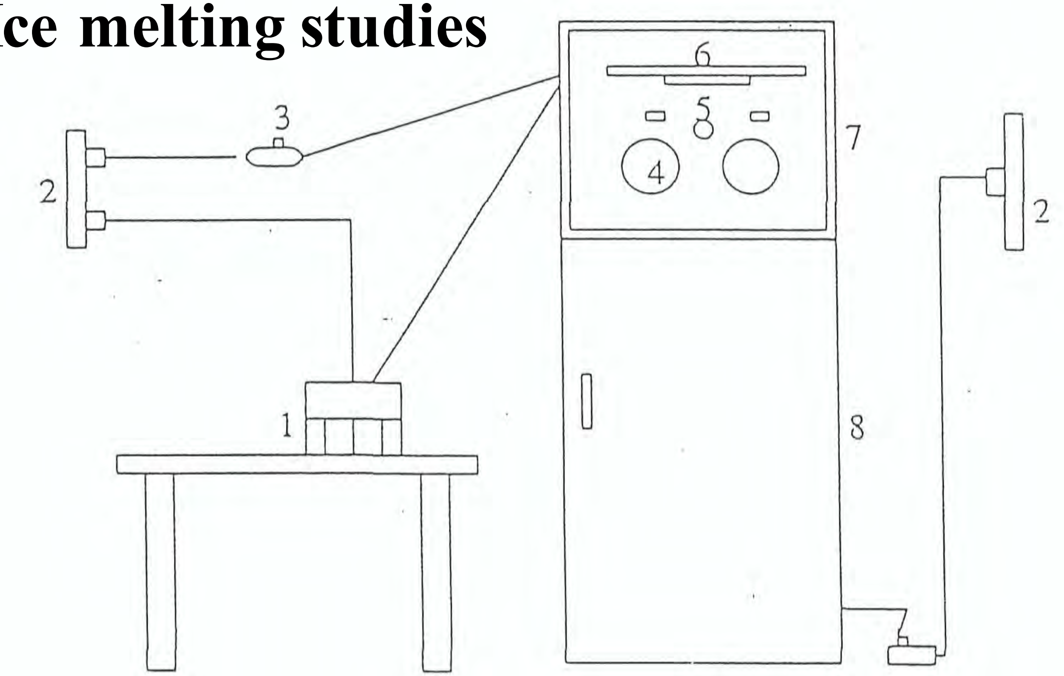
Experimental Methods

- CMA and CMP prepared by reacting acetic and propionic acids with Ca and Mg hydroxides
- Sludge-CMA and Sludge-CMP obtained by reacting filtered sludge with acetic and propionic acids
- Freezing point determination ANSI/ASTM D 1493-67 method
- Ice melting and ice penetration depth studies (Strategic Highway Research Program protocols)


CMA from softening
sludge slurry
CMA from dolomite

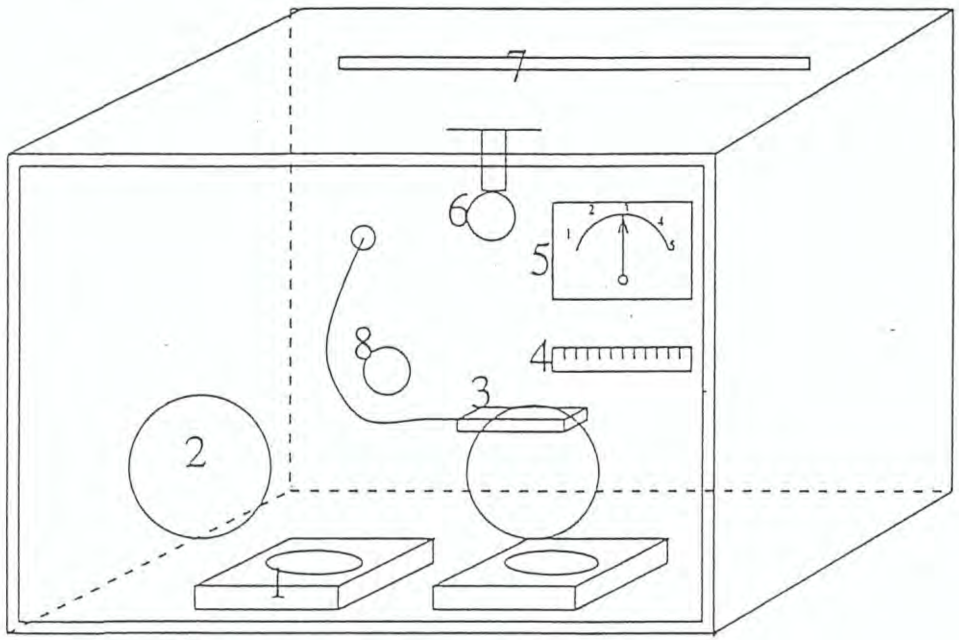

CMA from
sludge powder
Calcium acetate
from CaCO3

Ice melting studies



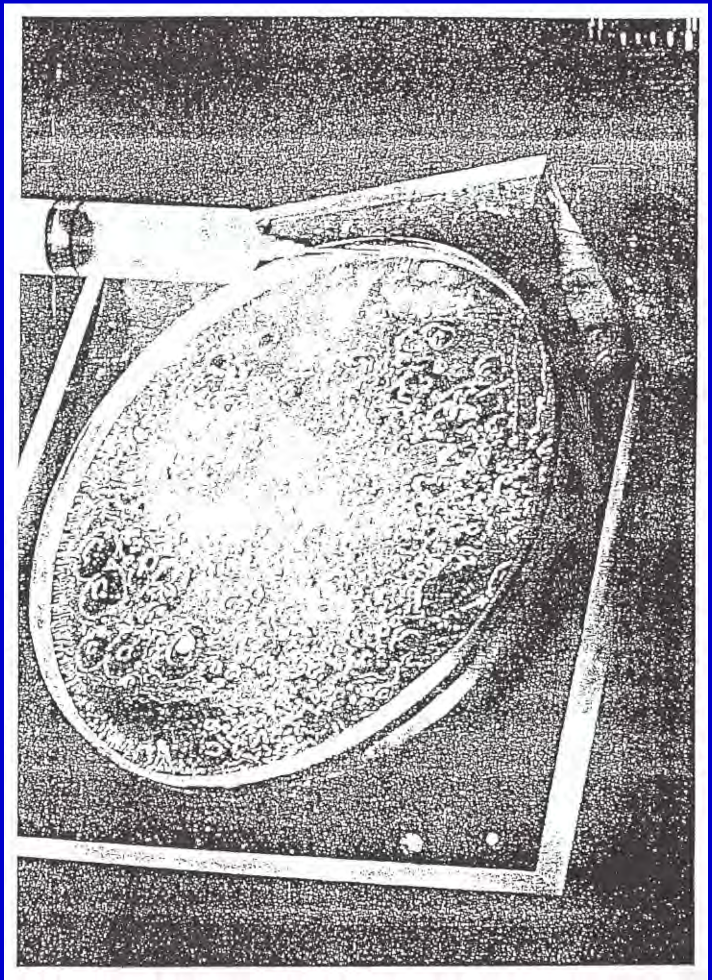
Experimental Set-Up

1. Temperature Controller
2. Power Supply
3. Switch
4. Access Holes
5. Peep-hole
6. Fluorescent lamp
7. Temp. controlled test enclosure
8. Refrigerator



Temp. controlled test enclosure

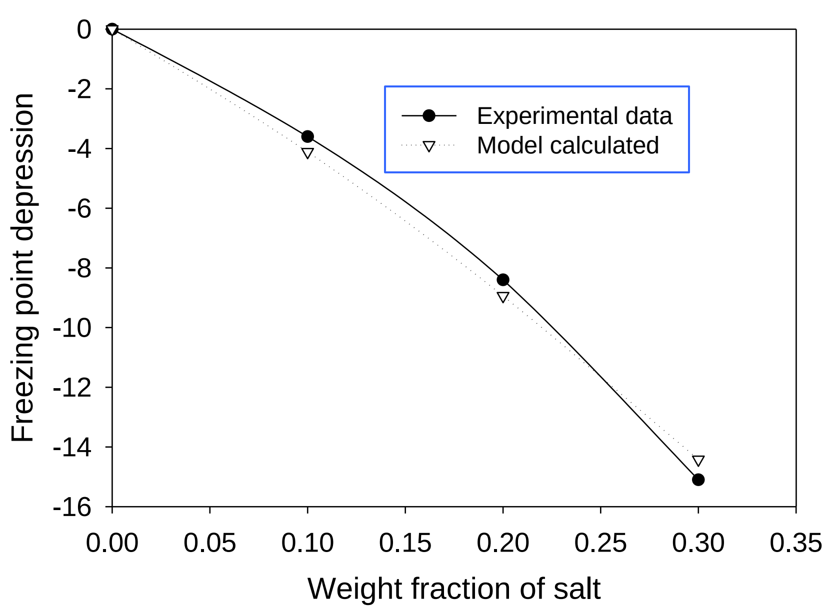
1. Plexi-glass test dish
2. Access hole
3. Thermo-couple
4. Wall thermometer
5. Freezer temp. control
6. Light bulb
7. Fluorescent lamp
8. Peep-hole



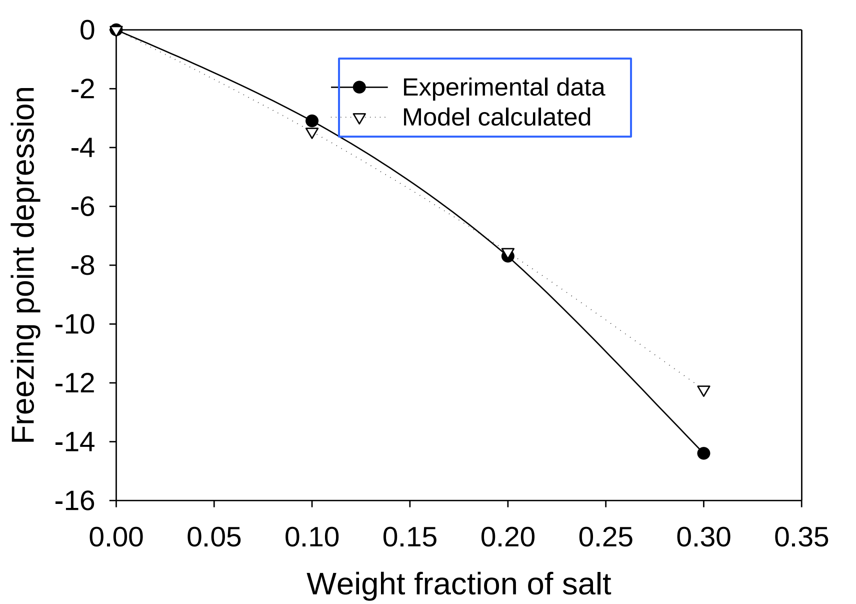
Ice melting rate determination

Ice melting penetration depth

Experimental and Modeling Results



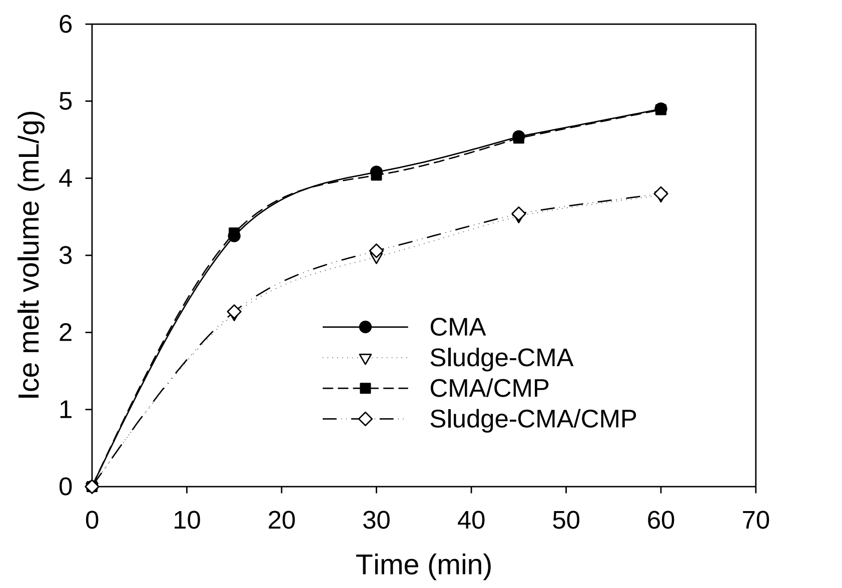
Freezing point depression: Model and data, CMA



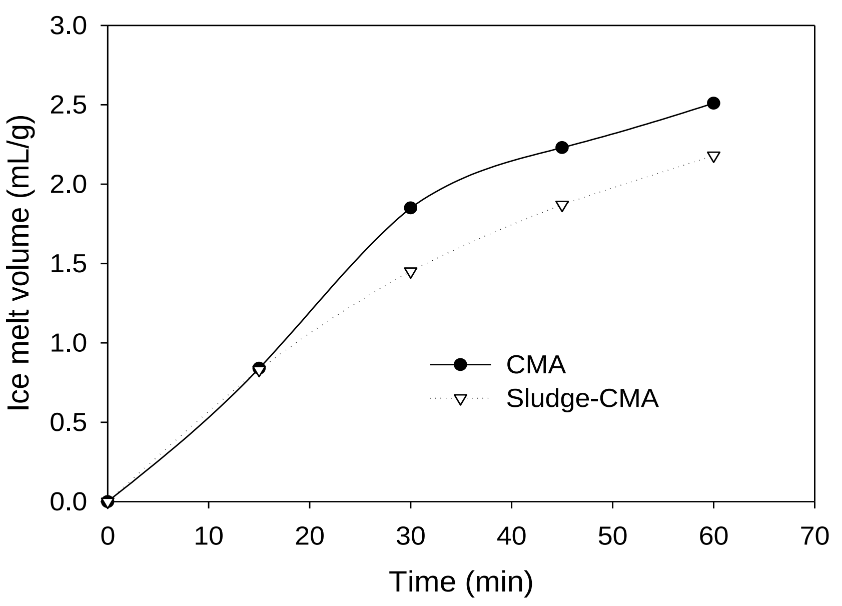
Freezing point depression: Model and data for CMP

Freezing point depression model predictions for CMA and CMP (Ca:Mg 3:7)

Ice melting rate studies



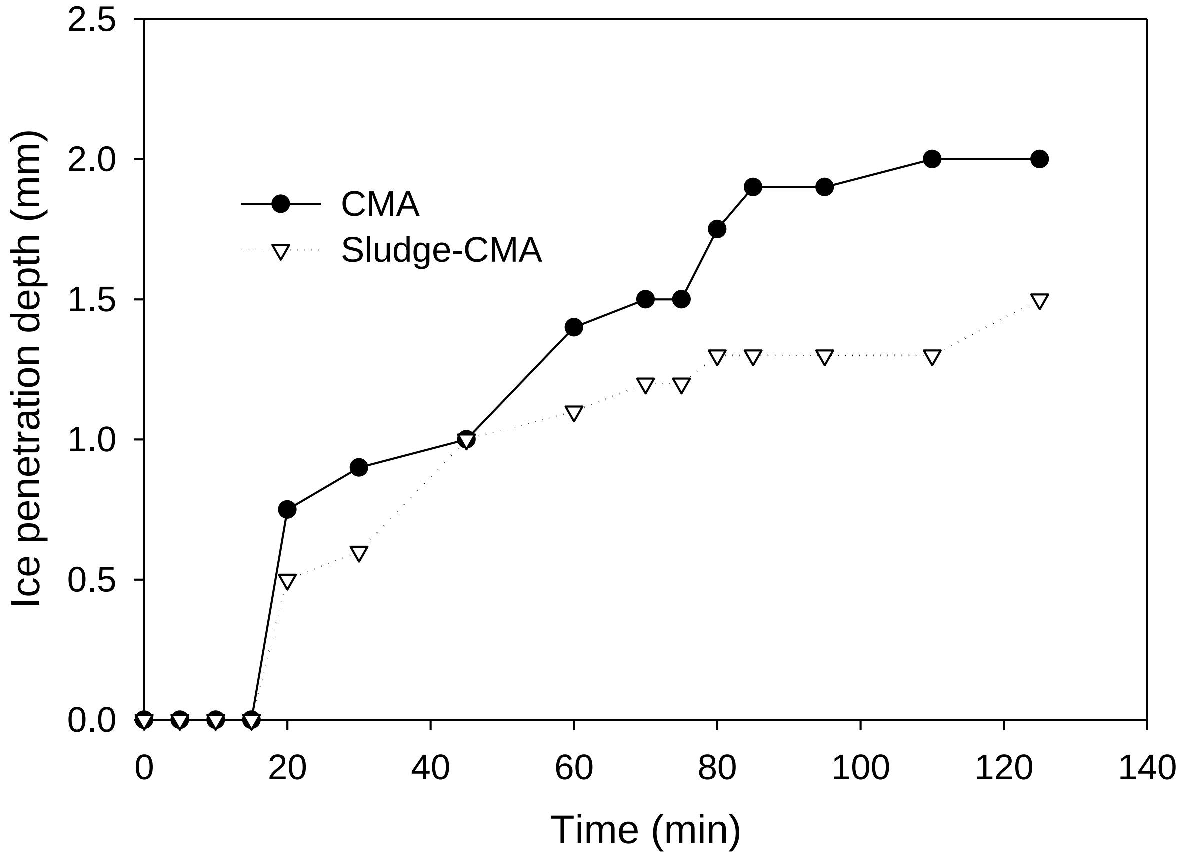
Ice melting rates CMA/CMP and sludge-decier at -7 C



Ice melting rates at -11.5 C

Ice melting rates at -7 C and -11.5 C for deicers

Ice penetration depth studies



Ice penetration depths at -11.5^{o} C

Conclusions

- CMA obtained from water softening sludge can be effectively used for road deicing

  Sludge-CMA deicer contains ~ 5 to 20% inerts

  Synthetic CMA: Ca to Mg mole ratio 3:7

  S-CMA: Ca to Mg mole ratio of ~ 9:1

  High Ca to Mg ratio **minimizes** concrete deterioration as Mg is expansive

- Theoretical FPD model based on estimation of electrolyte activities is accurate
- Model is useful for design of deicing salt mixtures

Conclusions

- Deicing salts are the largest contributors to the high chloride concentrations in freshwater systems
- There is an urgent need to protect freshwater biota and drinking water supplies from salt inputs
- Regulations to increase the use of substitute deicers that are biodegradable are needed
- Reuse of water softening residuals can help reduce the overall cost of CMA deicers
- Oxygen depletion effects of biodegradable deicers can be mitigated by using ORCs as additives

THANK YOU

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