



Experimental Work Conducted on MgO Characterization and Hydration

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Outline

- **Introduction**
- **Experimental work conducted on MgO**

MgO characterization

MgO hydration

- **Summary**



Waste Isolation Pilot Plant (WIPP)

- The Waste Isolation Pilot Plant (WIPP) is a U.S. Department of Energy repository for defense-related transuranic waste
- It is located in southeast New Mexico at a depth of 655 m in the Salado Formation, a Permian bedded-salt formation



Cutaway View of CH TRU Waste





Role of MgO

Functions as an engineered barrier by consuming CO_2 from possible microbial activity generated by the biodegradation of cellulosic, plastic, and rubber materials, thereby decreasing actinide solubilities

- Will react with CO_2 and H_2O in brine and water vapor to form hydrous and, eventually, anhydrous Mg carbonates
- Will control pH at mildly alkaline range

MgO recognized as the only engineered barrier in the WIPP disposal system in the EPA's 1998 certification of the WIPP



MgO Characterization

- Particle-size distribution
- Mineralogical composition (ICP-AES, SEM, EDS spectra)
- Quantitative analysis of the reactive constituents (loss on ignition and thermo gravimetric analysis on hydrated MgO)

MgO Particle-size Distribution by Sieving

Mesh #	Average (wt %)	Standard Deviation (wt %)	Wt % Passing Through the Sieve	Mesh #	Wt % Passing Sieve¹
> 10 (> 2.0 mm)	7.02	0.91	92.98	3/8 inch (9.5 mm)	100
10 - 18 (2.0 mm – 1.0 mm)	32.52	1.76	60.45	6 (3.4 mm)	99.9
18 - 30 (1.0 mm – 600 µm)	20.25	1.28	40.21	16 (1.18 mm)	73.1
30 - 50 (600 µm – 300 µm)	12.74	2.19	27.47	30 (600 µm)	41.6
50 - 100 (300 µm – 150 µm)	5.35	0.70	22.12	100 (150 µm)	21.3
100 - 200 (150 µm – 75 µm)	3.36	0.35	18.77		
< 200 (< 75 µm)	17.91	1.88			
Total	100	0			

1. Manufacturer's analysis sheet.



Concentration of Mg, Al, Si, Ca and Fe that dissolved in nitric acid

	MgO (wt %)	CaO (wt %)	Al ₂ O ₃ (wt %)	Fe ₂ O ₃ (wt %)	SiO ₂ (wt %)
Average	98.46	0.87	0.13	0.12	0.31
Standard Deviation	2.54	0.03	0.02	0.01	0.01

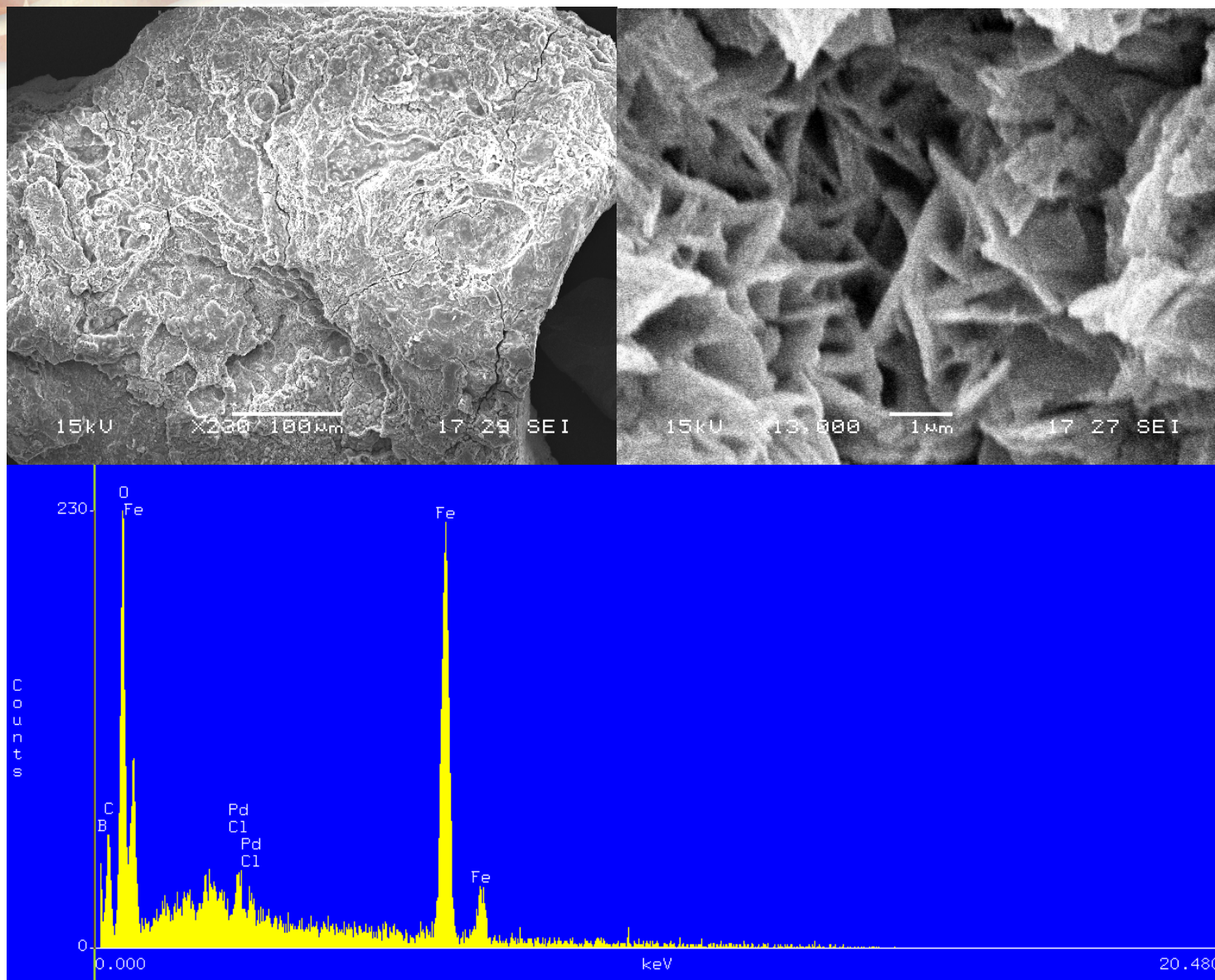
MgO, Al₂O₃, SiO₂, CaO and Fe₂O₃ are reported here as oxides, which aren't necessarily representative of the actual phases in the MM MgO

Weight fraction of periclase and lime in (unhydrated) MM MgO

	Average (wt %)	Standard Deviation (wt %)	Reported Value mean \pm σ (wt %)
periclase	94.8	1.72	95 \pm 2
lime	0.874	0.0256	0.87 \pm 0.03
periclase+lime	95.7	1.74	96 \pm 2

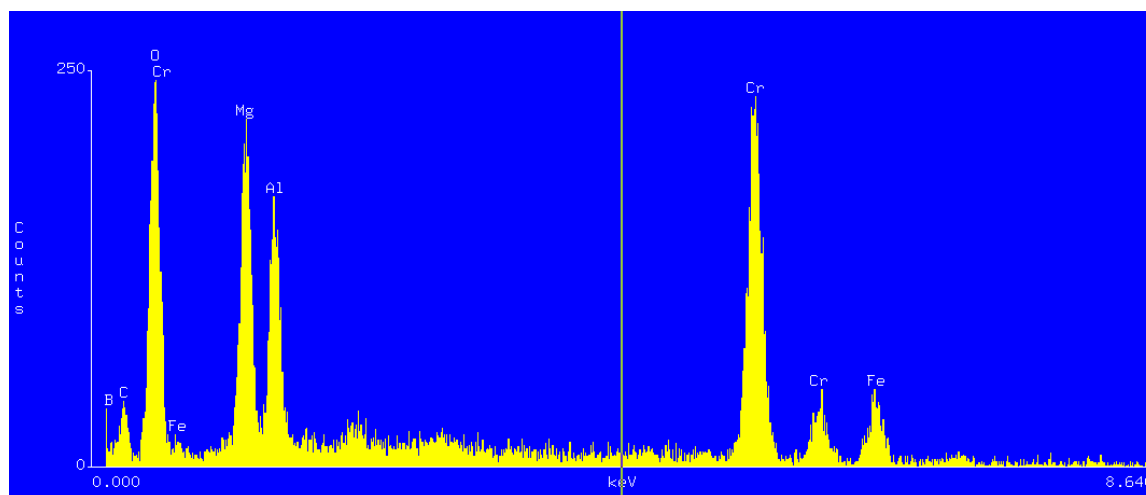
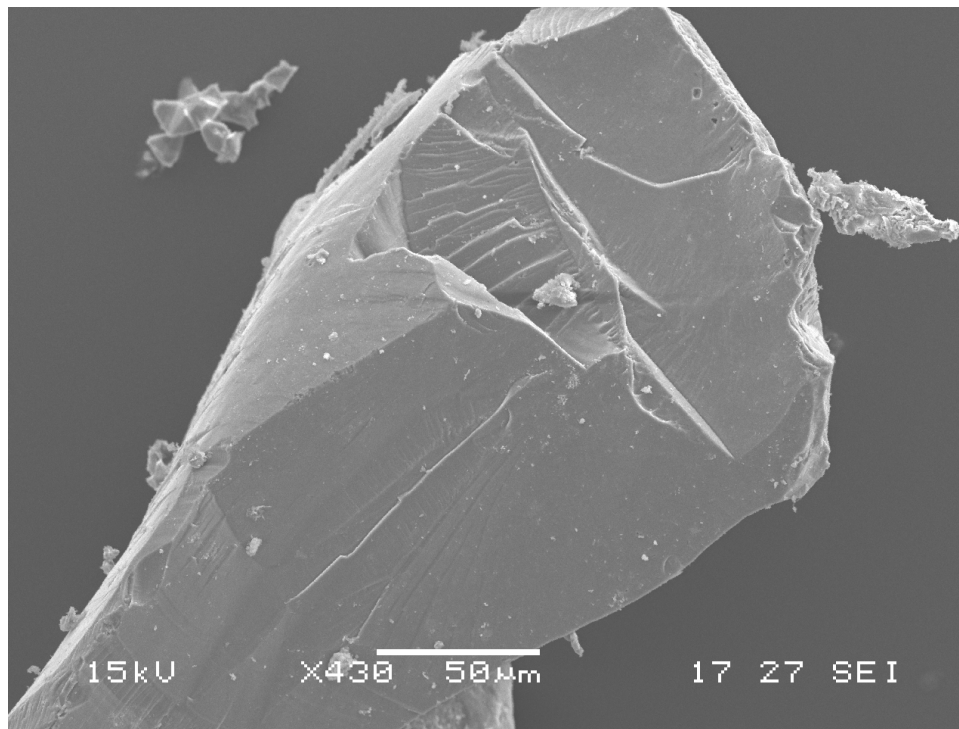
Premier MgO: 92 wt % of periclase + lime



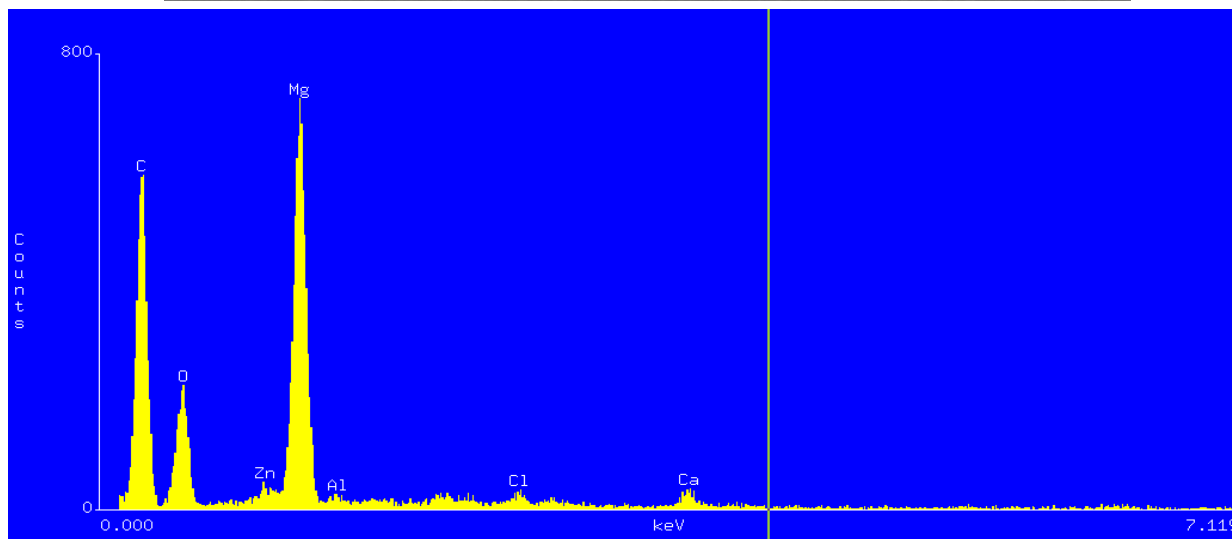
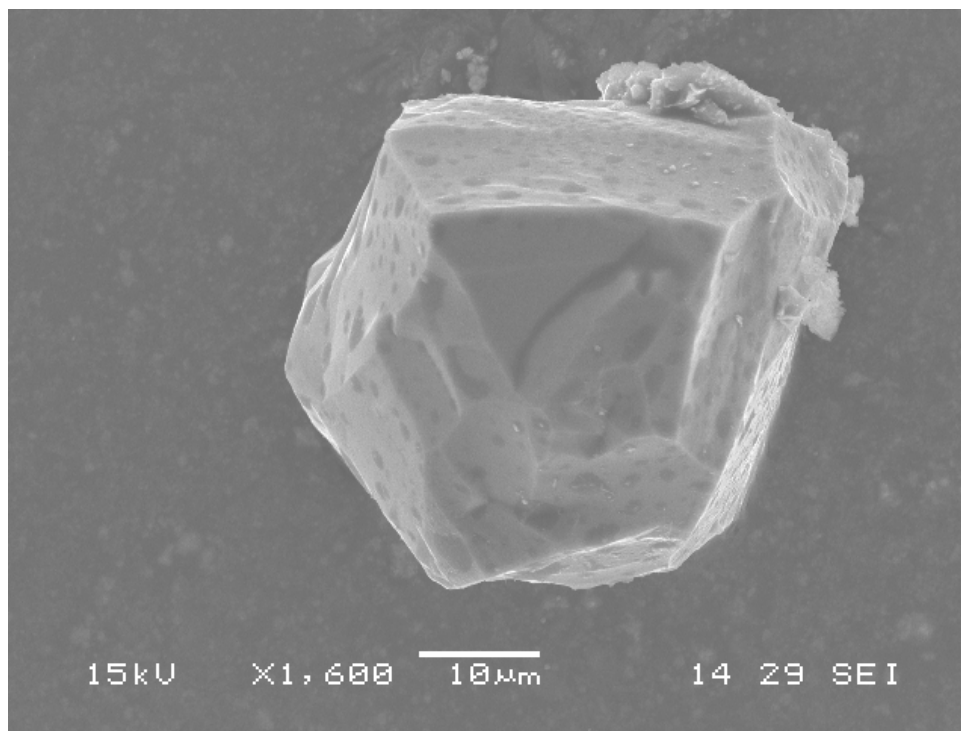


Impurities: iron oxide

Impurities: spinel



Refractory piece of MgO





MgO Hydration

- Humid Hydration
 - Accelerated humid hydration
 - Effect of particle size, temperature and relative humidity
 - Long-term humid hydration
- Inundated hydration
 - Accelerated inundated hydration
 - Effect of particle size, MgO/water ratio and stirring speed
 - Long-term inundated hydration



Accelerated inundated hydration experimental matrix

- Motion
 - still
 - 150 rpm
- Particle size
 - big particles 1.0-2.0 mm
 - small particles $<75\ \mu\text{m}$
- MgO/water ratio
 - 10 g of MM MgO with 10 mL of DI water
 - 8 g of MM MgO and 20 mL of DI water
 - 5 g of MM MgO and 100mL of DI water

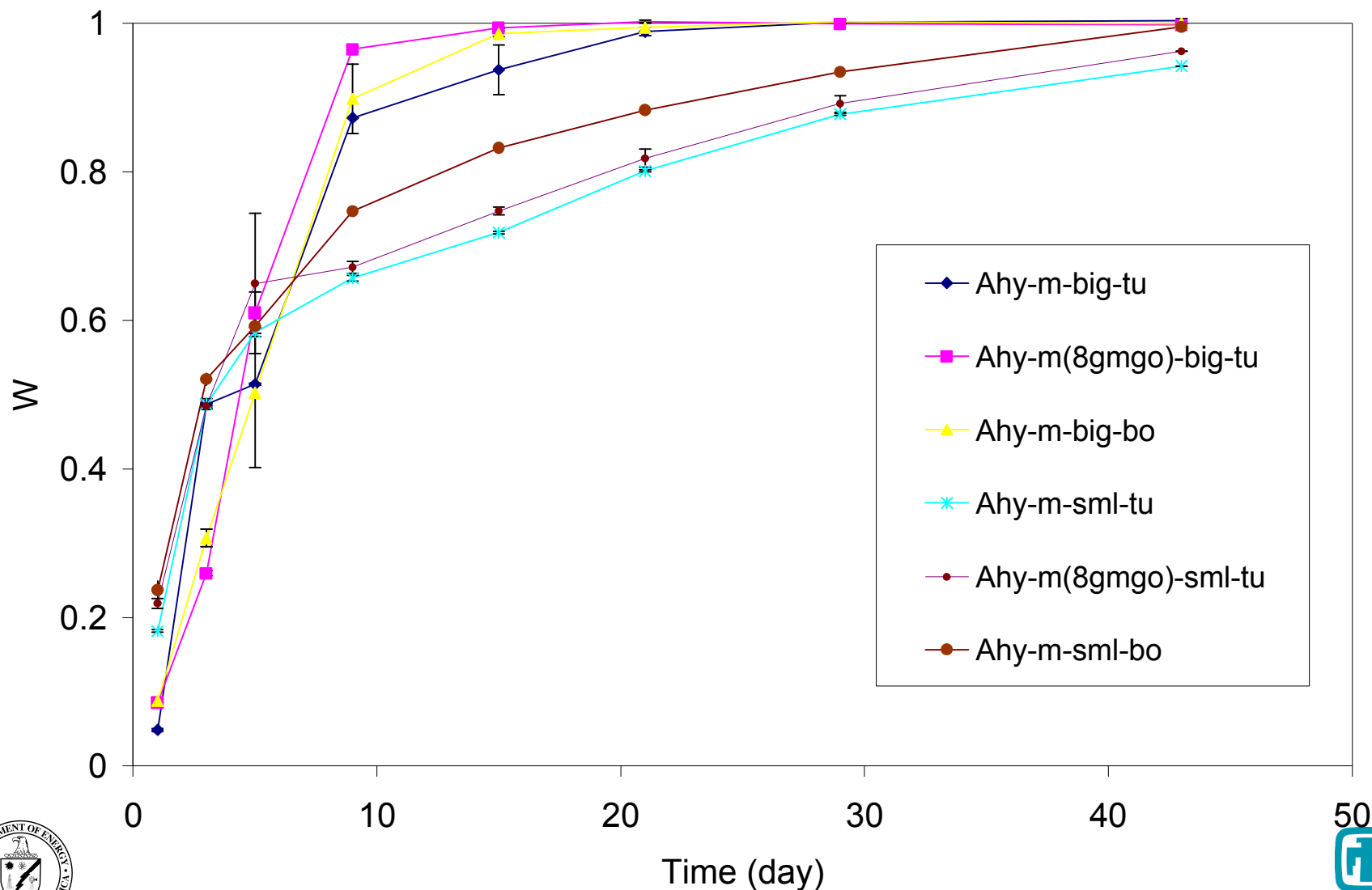


Factors affecting the hydration rate

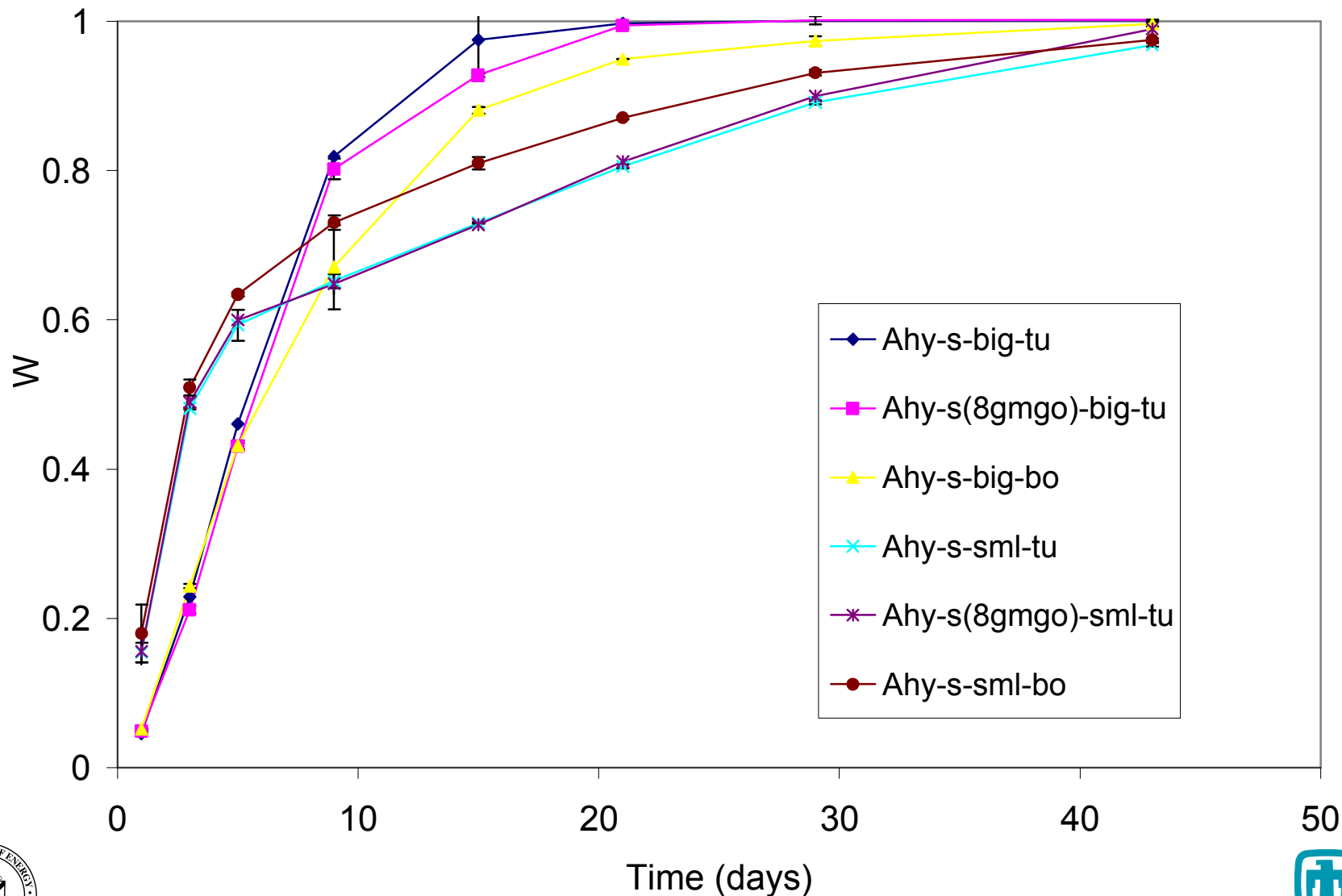
- As hydration proceeds, shaking becomes less important but particle size is always a critical factor
- MgO/water ratio becomes increasingly important as hydration proceeds



MM MgO hydration progress (W) versus time (days) for experiments carried out in DI water at 70 °C in an oven (not shaken)



MM MgO hydration progress (W) versus time experiments carried out in water bath shaker at 70 °C at a shaking speed of 150 rpm



Comparison with theoretical kinetic models

- Surface-controlled model

$$y_1 = 1 - (1 - W)^{1/3} = k_1 t.$$

- Diffusion-controlled models

$$y_2 = \left[1 - (1 - W)^{1/3} \right]^2 = k_2 t$$

$$y_3 = \frac{\left[1 + (z - 1)W \right]^{2/3} + (z - 1)(1 - W)^{2/3} - z}{2(1 - z)} = k_3 t$$

$$y_4 = 1 - 2/3 W - (1 - W)^{2/3} = k_4 t$$



MgO Carbonation

- Chemical solution phase control of P_{CO_2}
- Environmental chamber with fixed humidity and P_{CO_2}



Summary

- The concentration of reactive components (periclase plus lime) in MM MgO, 96 ± 2 wt %, is higher than that of Premier MgO, 92 wt %
- MgO particle size has an important effect on the rate of MgO hydration process

Backup slides

