Value-Added Use of Large CO_2 Volumes for Production of Hydraulic Cement

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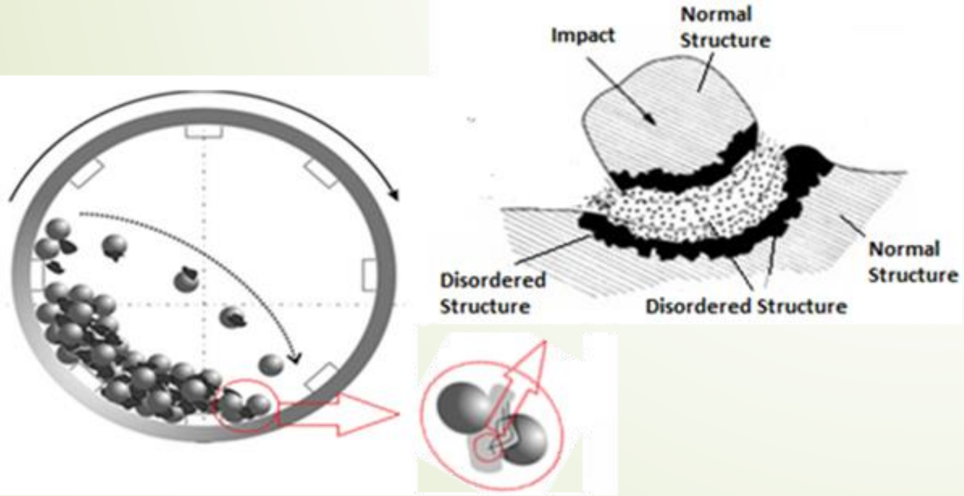
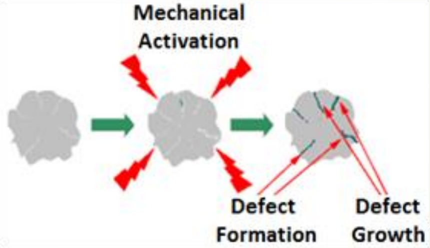
Hydraulic Cements

- Portland cement is prevalent, used primarily for concrete production
- Massive and growing consumption of cement, >4 billion tons/yr
- Energy-intensive and polluting production, releasing ~3.6 billion tons/yr CO_2
- The alkaline chemistry of Portland cement makes 'carbonation' reactions detrimental, mitigating value-added and large-volume use of CO_2
- Quantitative gains in the sustainability of Portland cement production have been realized by improving the energy-efficiency of various processes
- Qualitative gains in sustainability and value-added use of CO_2 arguably require the use of alternative hydraulic cement chemistries
- Different cement chemistries were explored; the focus here is on a low-pH one that makes value-added use of the CO_2 content of combustion emissions

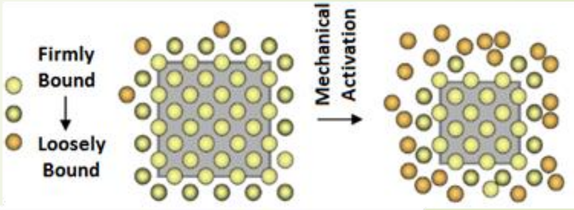
Mechanochemistry: An Alternative to High-Temperature Processing of cement

- Pyro-processing (at elevated temperature) of Portland cement requires combustion of fossil fuels, which accounts for 75% of energy use
- Mechanochemistry: Chemical and physicochemical changes of substances induced by input of mechanical energy
- Mechanochemical processing relies upon instantaneous and intense local phenomena which occur at the point of impact in simple milling operations at room temperature and atmospheric pressure





Defect Formation & Growth

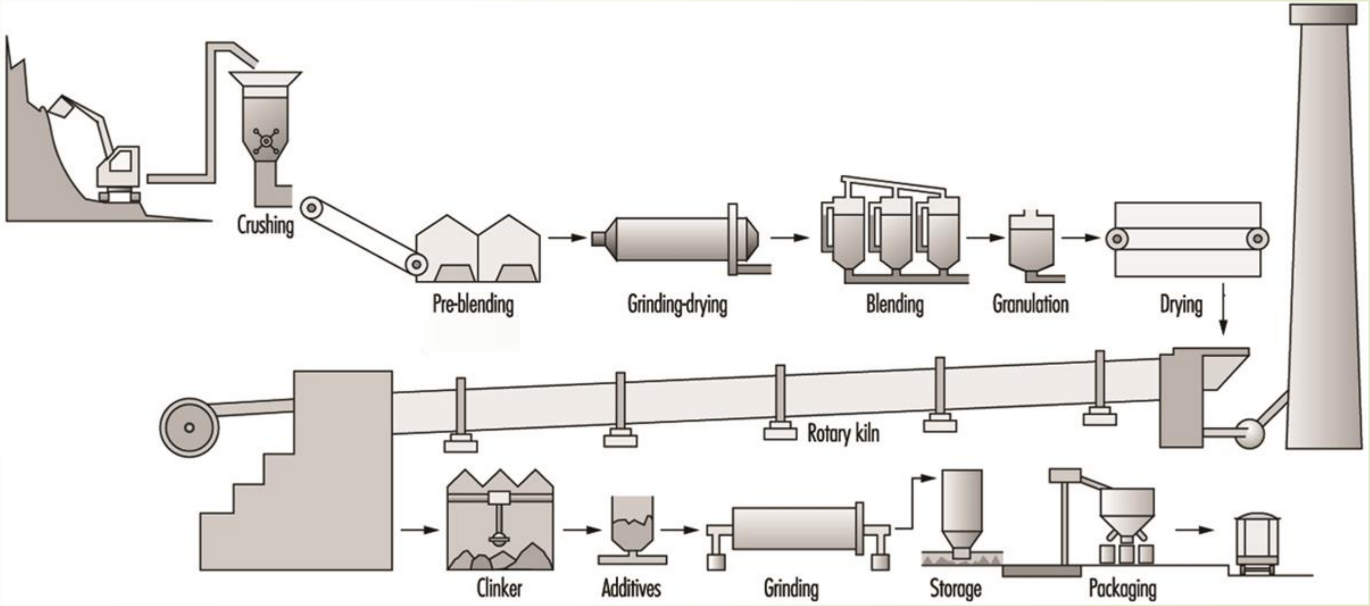


Amorphization

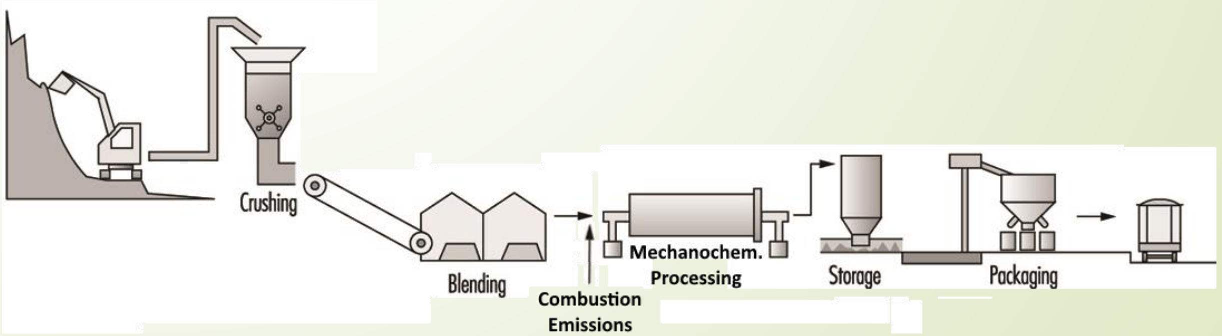
Mechanochemical Reactions

Simplified Mechanochemical Processing of Cement

Conventional:



Mechanochemical:



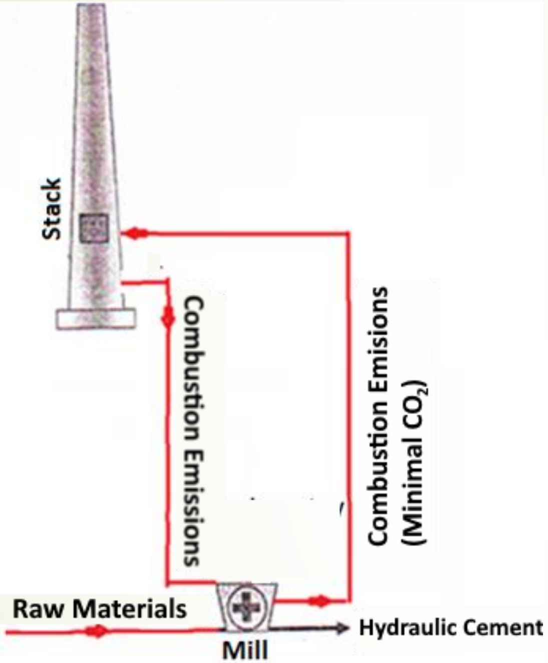
Example Cement Chemistries and Carbonation Effects

- Portland cement
  - $2\ Ca_3SiO_5 + 7\ H_2O \rightarrow 3CaO\ .\ 2SiO_2\ .\ 4H_2O + 3\ Ca(OH)_2$
  - Carbonation has detrimental effects: (i) pH drop; (ii) decomposition of calcium silicate hydrate

- A low-pH hydraulic cement
  - $3Ca_4.(PO_4)_2.O + 2H_2O \rightarrow Ca_{10}.(PO_4)_6.(OH)_2 + Ca(OH)_2$
  - Carbonation has beneficial effects: (i) mitigation of pH rise; (ii) transformation of hydroxyapatite into carbonate apatite

Pilot-Scale Production of a Low-pH Hydraulic Cement in Combustion Emissions

Power Plant



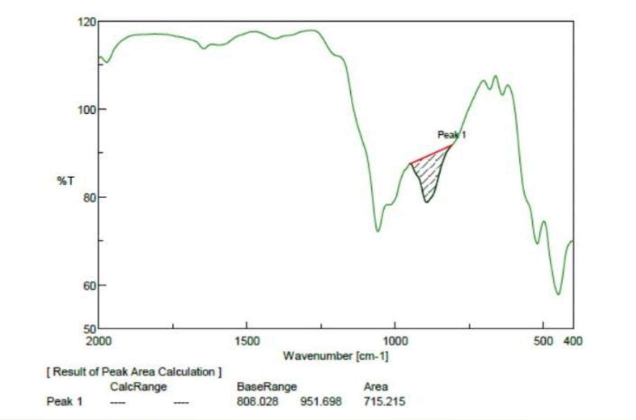
Representative Conditions

Properties of Combustion Emissions & Hydraulic Cements

- Inlet & Outlet Properties of Combustion Emissions

Property	Inlet	Outlet
CO_2 Concentration, %	7.4	1.4
Temperature, °C	51.8	32.7
Relative Humidity, %	100.0	51.2

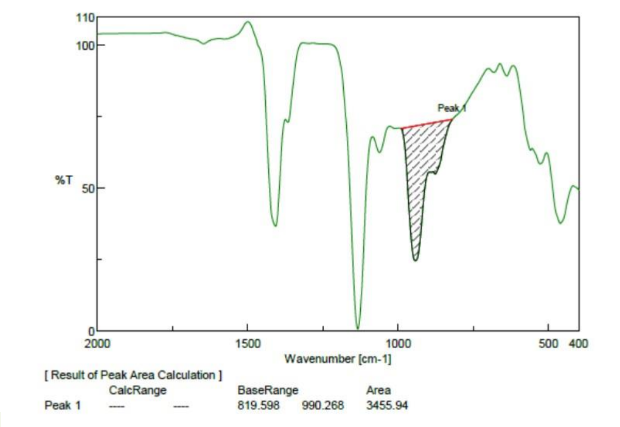
- Cement Properties: FTIR Peak for Carbonate Apatite, and pH & TDS



[Result of Peak Area Calculation]

	CalcRange		BaseRange		Area
Peak 1	----	----	808.028	951.698	715.215

Air



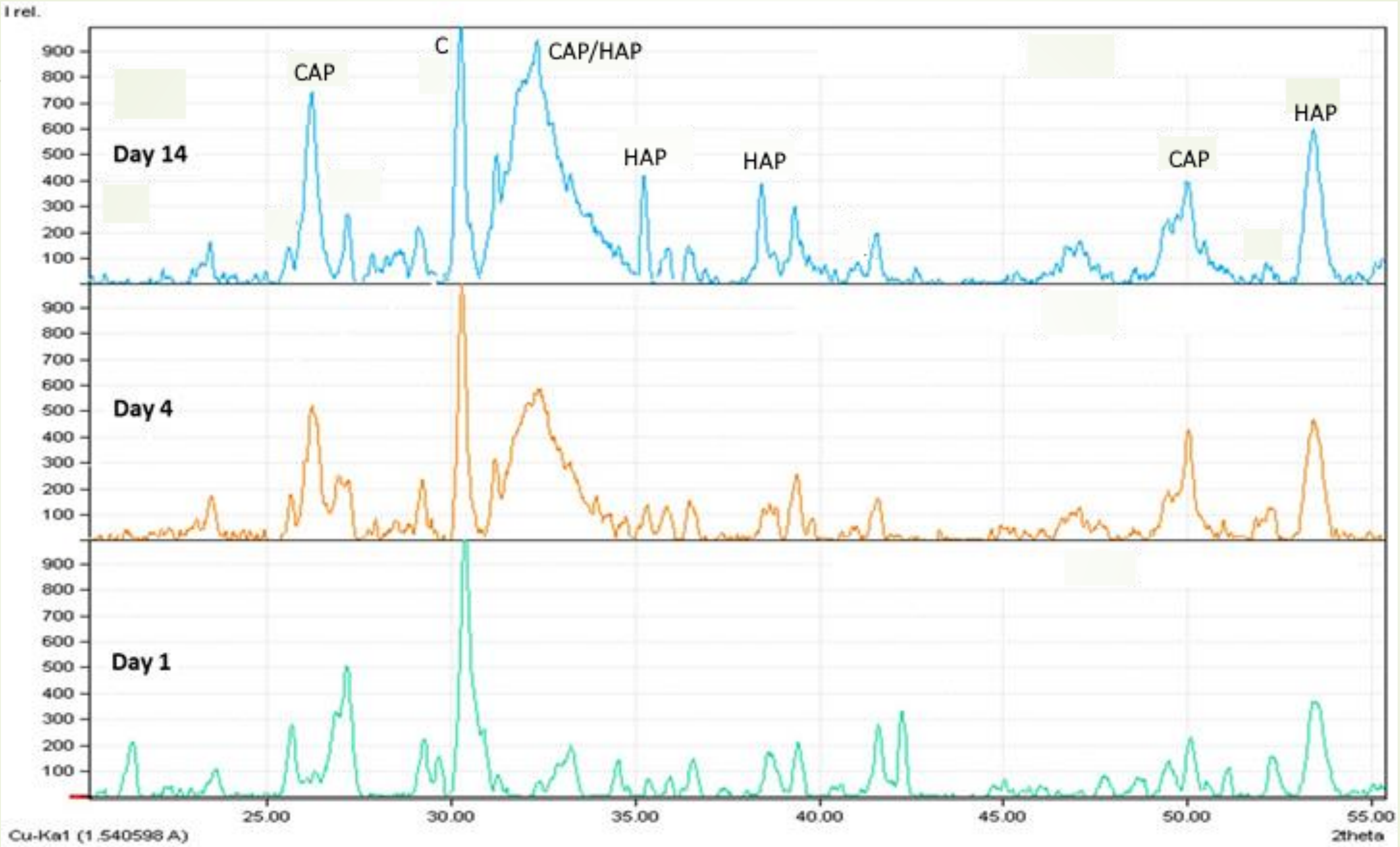
[Result of Peak Area Calculation]

	CalcRange		BaseRange		Area
Peak 1	----	----	819.598	990.268	3455.94

CO_2

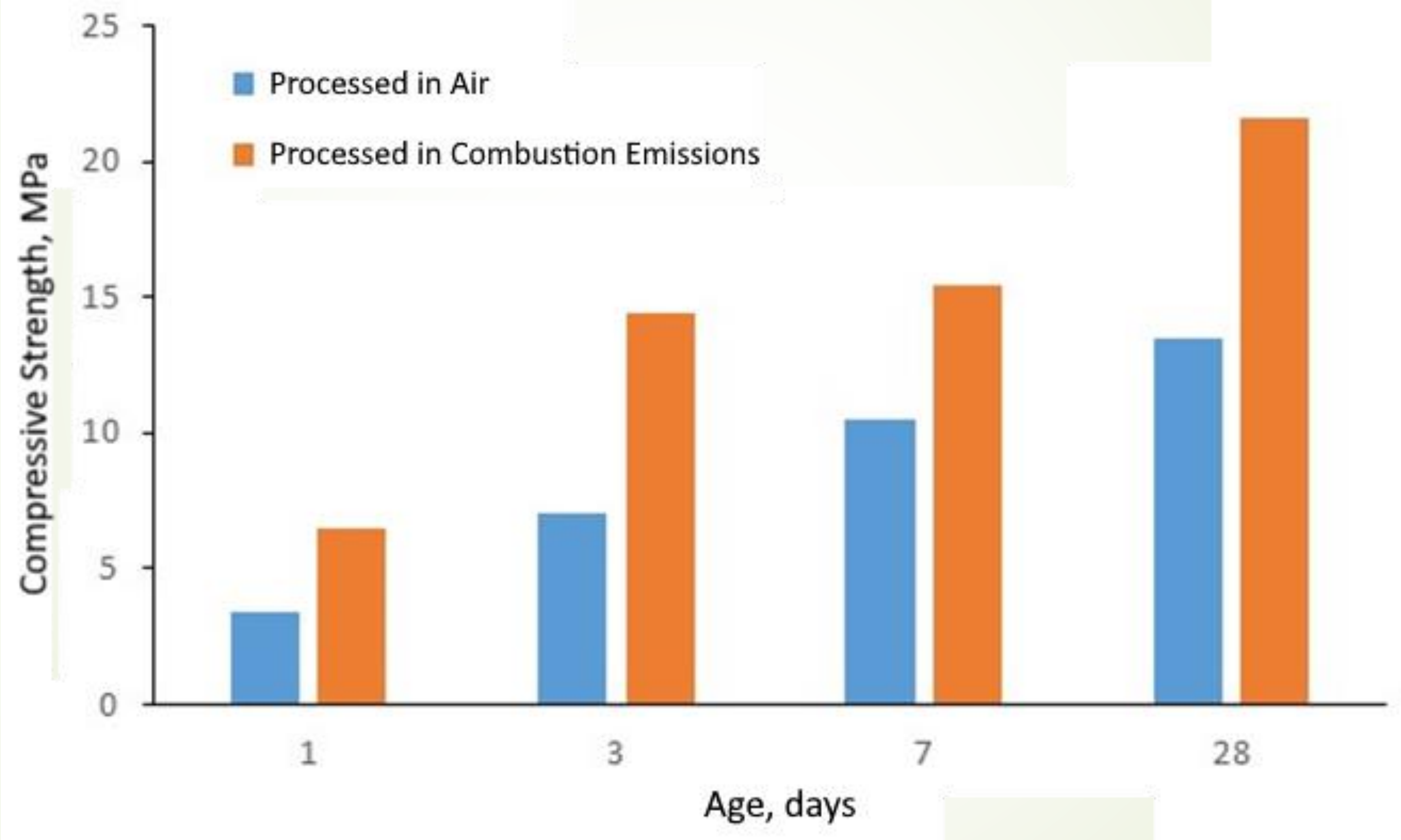
Processing Environment	pH	TDS, ppm
Air	7.61	674.0
CO2	6.58	996.4

XRD Spectra of Hydrating Cement

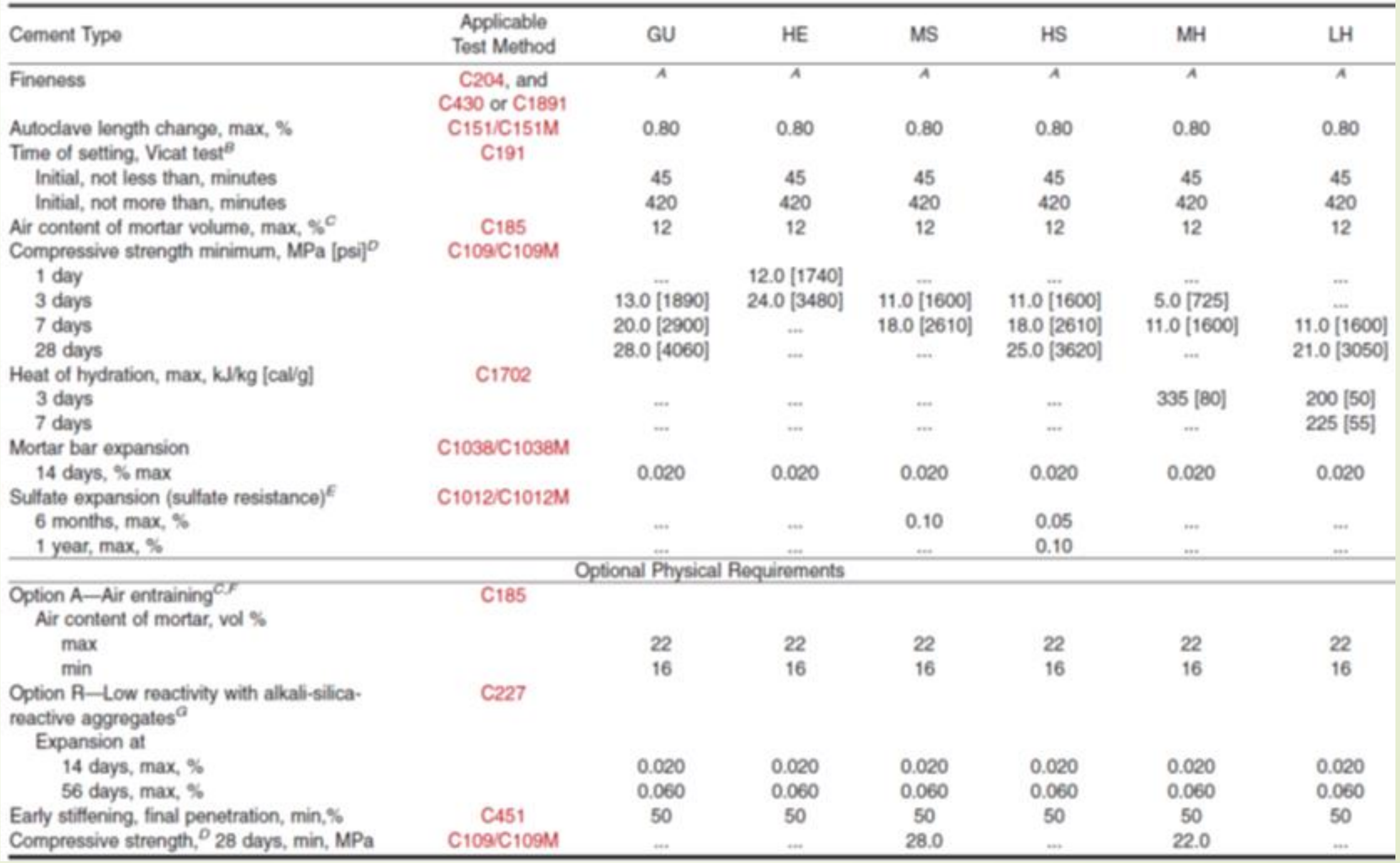


Mineral	Curing Time, days		
	1	4	14
Calcite	2.4%	3.9%	4.2%
Hydroxyapatite	3.8%	19.3%	34.9%
Carbonate Apatite	2.1%	23.6%	44.5%

Strength Development with Time



The New Hydraulic Cement Meets the ASTM C1157 Performance-Based Requirements



Cement Type	Applicable Test Method	GU	HE	MS	HS	MH	LH
Fineness	C204, and C430 or C1891	[A]	[A]	[A]	[A]	[A]	[A]
Autoclave length change, max, %	C151/C151M	0.80	0.80	0.80	0.80	0.80	0.80
Time of setting, Vicat test[B]	C191						
Initial, not less than, minutes		45	45	45	45	45	45
Initial, not more than, minutes		420	420	420	420	420	420
Air content of mortar volume, max, %[C]	C185	12	12	12	12	12	12
Compressive strength minimum, MPa [psi][D]	C109/C109M						
1 day		...	12.0 [1740]	...	...	...	...
3 days		13.0 [1890]	24.0 [3480]	11.0 [1600]	11.0 [1600]	5.0 [725]	...
7 days		20.0 [2900]	...	18.0 [2610]	18.0 [2610]	11.0 [1600]	11.0 [1600]
28 days		28.0 [4060]	...	...	25.0 [3620]	...	21.0 [3050]
Heat of hydration, max, kJ/kg [cal/g]	C1702						
3 days		...	...	...	...	335 [80]	200 [50]
7 days		...	...	...	...	...	225 [55]
Mortar bar expansion	C1038/C1038M						
14 days, % max		0.020	0.020	0.020	0.020	0.020	0.020
Sulfate expansion (sulfate resistance)[E]	C1012/C1012M						
6 months, max, %		...	...	0.10	0.05	...	...
1 year, max, %		...	...	...	0.10	...	...
Optional Physical Requirements							
Option A—Air entraining[C,F]	C185						
Air content of mortar, vol %							
max		22	22	22	22	22	22
min		16	16	16	16	16	16
Option R—Low reactivity with alkali-silica-reactive aggregates[G]	C227						
Expansion at							
14 days, max, %		0.020	0.020	0.020	0.020	0.020	0.020
56 days, max, %		0.060	0.060	0.060	0.060	0.060	0.060
Early stiffening, final penetration, min,%	C451	50	50	50	50	50	50
Compressive strength,[D] 28 days, min, MPa	C109/C109M	...	...	28.0	...	22.0	...

Energy Content and Carbon Footprint

- Energy Contents in Laboratory and Pilot Scale Processing

Scale	Specific Energy, kJ/kg	Specific Energy per Unit Strength, kJ/(kg.MPa)
Laboratory	10,836	0.474
Pilot	1,623	0.042

- Net CO_2 Signatures in Industrial-Scale Processing
  - New Cement: ~0.02 ton per ton of hydraulic cement
  - Portland Cement: ~0.9 ton per ton of hydraulic cement

Conclusions

- Selection of cement chemistry is critical for value-added use of carbon dioxide as a raw material in production of hydraulic cements
- Mechanochemical processing can significantly reduce the energy demand in industrial-scale production of hydraulic cements, and can eliminate the need for combustion of fossil fuels to generate thermal energy
- Carbon dioxide can be (preferably) captured directly from combustion emissions in the course of mechanochemical processing of hydraulic cements
- With proper selection of cement chemistry, the end product quality improves with mechanochemical processing performed in combustion emissions vs. air
- Industrial-scale processing in combustion emissions can produce hydraulic cements with significantly reduced carbon footprint, energy demand and cost
- Mechanochemical processing can realize its full potential when implemented at industrial scale