MgO and other chemicals from Olivine $(Mg,_{Fe})_2SiO_4$

Feasibility and Technical Options

Concepts and objectives

In this presentation, olivine is introduced as an economically interesting, alternative starting material to produce

- high quality magnesium metal,
- magnesium refractories,
- fertilizer components and
- base material for pure magnesium chemicals.

Focus is mainly on magnesium raw materials for Mg metal production.

Magnesiopedia – incomplete

Magnesium is the 8th most abundant element in the Earth's Crust, with a global average of 2.1%. In the Earth's Mantle, the concentration is more than10 times this, i.e. 22.2 %. It is the third most abundant element dissolved in seawater with a concentration averaging around 0.14% by weight. In the entire universe, Mg is the 11th most abundant element (0.06%).[1)]

The bulk of magnesium oxide minerals (MgO)are sold in 3 varieties:

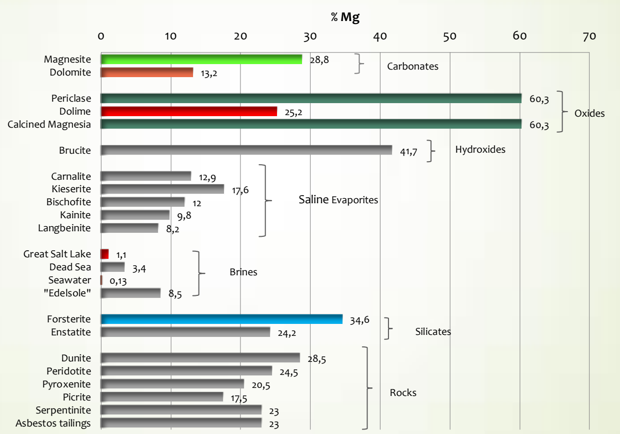
- caustic calcined magnesia (CCM),
- dead-burned magnesia (DBM) and
- electro fused magnesia (EFM).

Only CCM which has the largest and therefore most reactive surface area is technically suited to be used for magnesium metal production.
The present prevailing production method for magnesium metal requires a 50/50 mixture of calcium and magnesium oxide, obtained by calcination of dolomite.

1): Source::http://periodictable.com/Properties/A/UniverseAbundance.v.log.htm

Why MgO from Forsterite /Olivine?

Theoretical Mg Content in Magnesium-enriched Materials

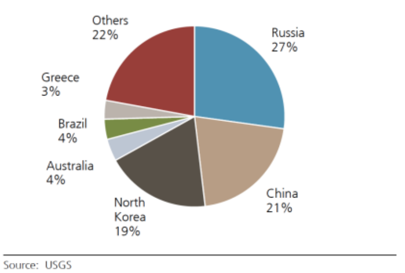


World overview, Magnesia and Olivine

	In Million tonnes			in %	
Product type	Production China	ROW	Total	China	ROW
CCM	3,94	1,43	5,37	73	27
DBM	3,52	2,94	6,46	54	46
FM	1,33	0,16	1,49	89	11
TOTAL MgO	8,79	4,53	13,32	66	34
Olivine	0,5	8,03	8,53	5,9	94,1
				Norway	**ROW**
Norway	3,5	4,53	8,53	41	59

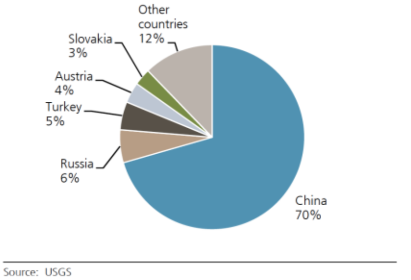
Source: Industry sources and China data from CCCMC, 2015

Figure 1: Magnesite reserves

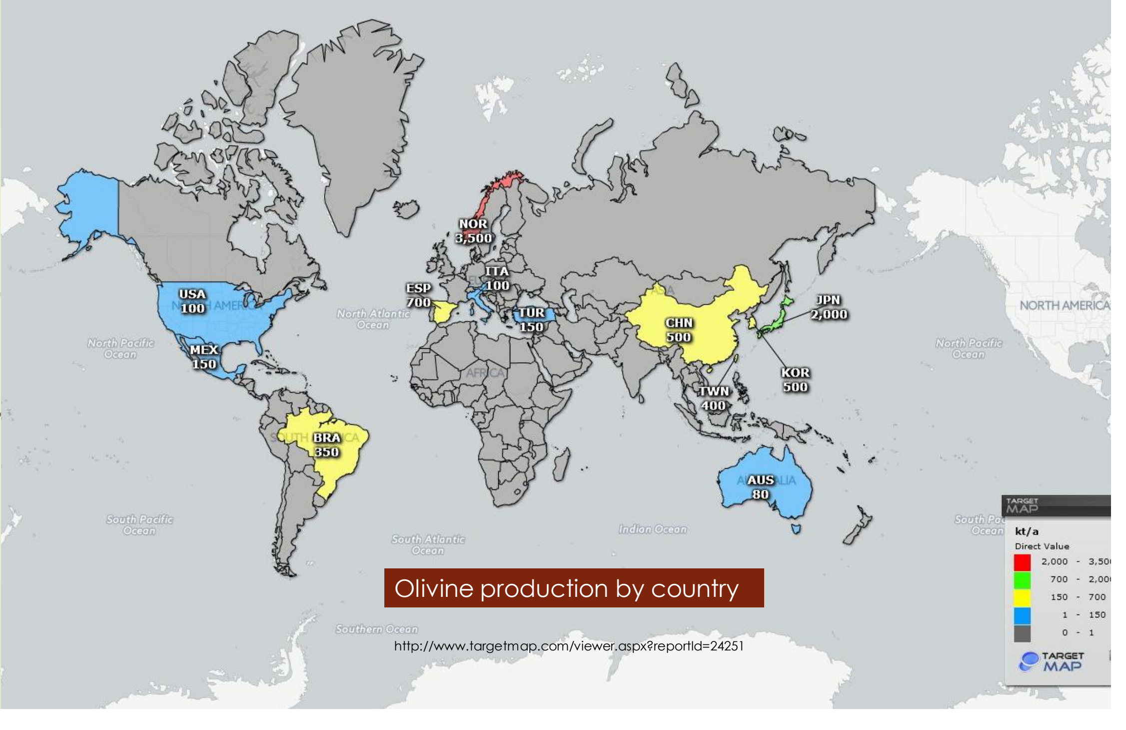


Source: USGS

Figure 2: Magnesite producers



Source: USGS



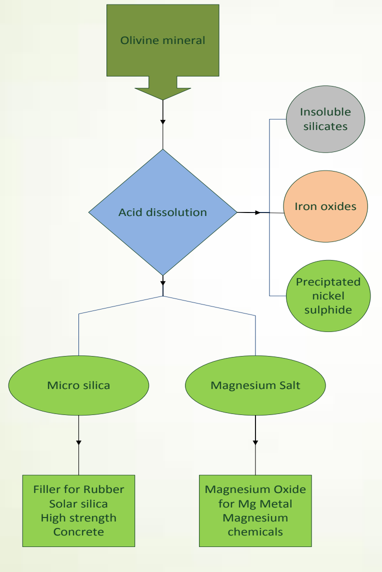
Olivine and Magnesia (MgO) Compositions
Traded Commodities

Sample	SiO2	TiO2	Al2O3	Fe2O3	FeO	MnO	MgO	CaO	Na2O	K2O	P2O5	Volat	Sum,maj.
Olivine	40,90	0,05	0,28	0,36	6,08	0,09	49,78	0,06	0,06	0,02	0,01	0,91	98,60
MgO 11, calcined	1,16	0,00	0,10	0,21	0,03	0,05	92,34	1,93	0,04	0,01	0,15	2,91	98,94
Magnesite, Nepal	1,54		0,49	1,83			45,91	0,36					

	V	Cr	Ni	Cu	Zn	Sr	La	Sum,Trace	Total
Olivine	8	1526	2792	7	17	30	0	4379	99,04
MgO 11	1	28	0	6	96	49	3	182	98,96

Focus Elements

Olivine Processing – conceptual Outline



Leaching Olivine:
Processing of olivine entails a leaching process which in principle can be done with any of the mineral acids - or as we shall see with other strongly acid compounds, or even with carbonic acid (with a little help).

After acid digestion, the insoluble solids will largely be micro silica, which is extensively used in concrete constructions. From the solute, Nickel and iron can be precipitated out, leaving only magnesium salt in the solution. The magnesium salt can be recovered by removing the water. If used for magnesium production an additional step which produces MgO and recover the acid for recycling is necessary.

Desirable Processing Attributes

- Low Cost
- Minimium Wastes / Green
- Proven Process
- No or few difficult unit operations
- Low CO_2 footprint

Selected Possible Route

- NH_4HSO_4 ammonium-bi- sulfate leaching is a patented process*(expired), but has not been commercialized.
- Advantageous because recycling of the reagent is straight-forward and low cost and offers flexibility in production lay-out

*A patent by Frederick L. Pundsack (U.S. 3,338,667, 1967) called the "Recovery of Silica, Iron Oxide and Magnesium Carbonate from the Treatment of Serpentine with Ammonium Bisulfate"

NH_4HSO_4 -Ammonium BiSulfate

What is ammonium bisulfate?
How is it made?

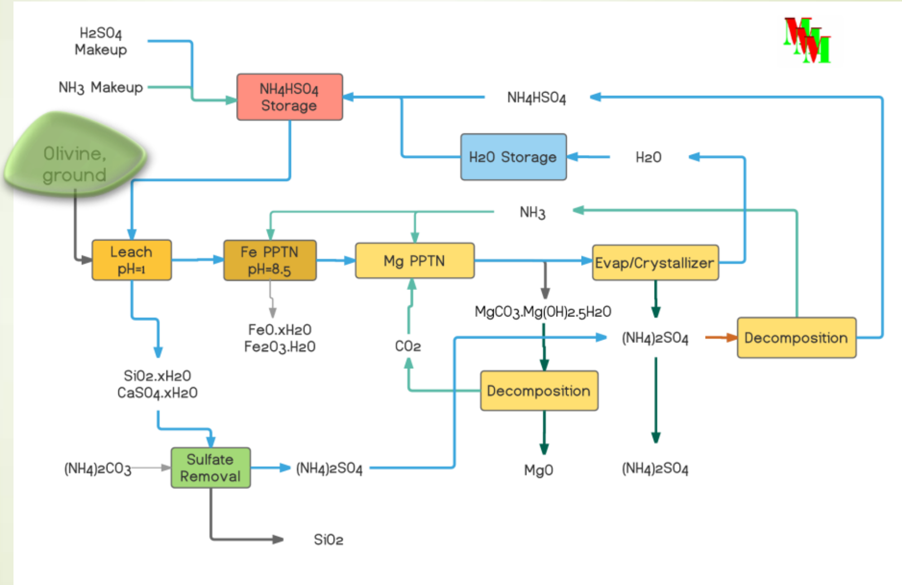
$NH_3 + H_2SO_4 \rightarrow NH_4HSO_4$

17 units of NH_3
98 units of H_2SO_4

A concentrated solution has a pH ~ 1

Properties	
Chemical formula	$(NH_4)HSO_4$
Molar mass	115.11 g/mol
Appearance	White solid
Density	1.78 g/cm^3
Melting point	147 °C (297 °F; 420 K)
Solubility in water	Very soluble
Solubility in other solvents	Soluble in methanol insoluble in acetone

Conceptual flowsheet Ammoniumbisulphate leaching



Leaching

Leaching Variables:

- Temperature
- Mesh size / particle size
- Excess acid/reagent
- Agitation
- Time

Note:
$(MgO.FeO)SiO_4$ treated as MgO, FeO and SiO_2 in reactions

SiO_2 will be "inert"

Major Leaching Reactions

$MgO + 2NH_4HSO_4 \rightarrow MgSO_4 + (NH_4)_2SO_4 + H_2O$

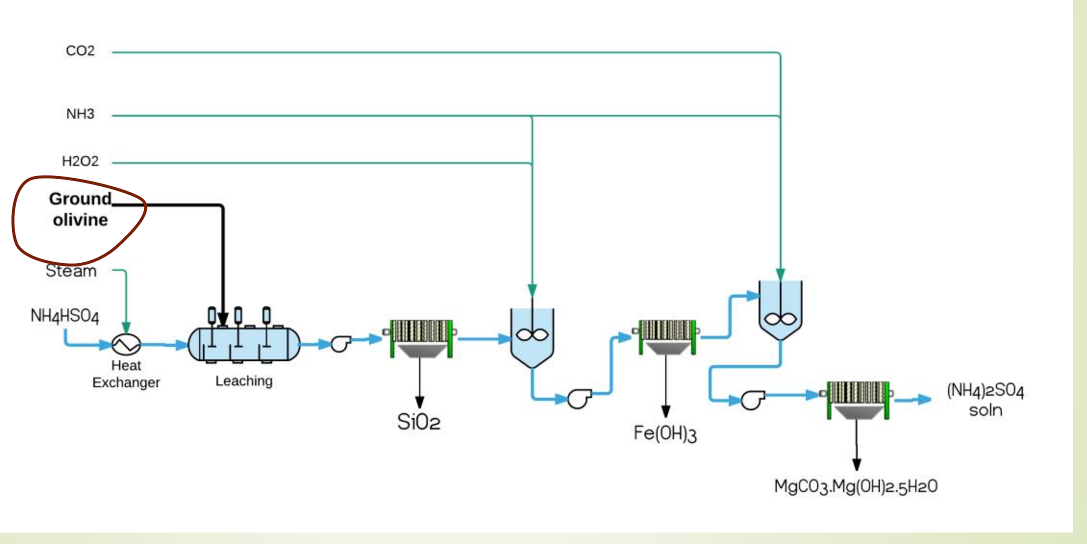
$FeO + 2NH_4HSO4 \rightarrow FeSO_4 + (NH_4)2SO_4 + H_2O$

$Fe_2O_3 + 6\ NH_4HSO4 \rightarrow Fe_2(SO_4)_3 + 3\ (NH_4)_2SO_4 + 3H_2O$

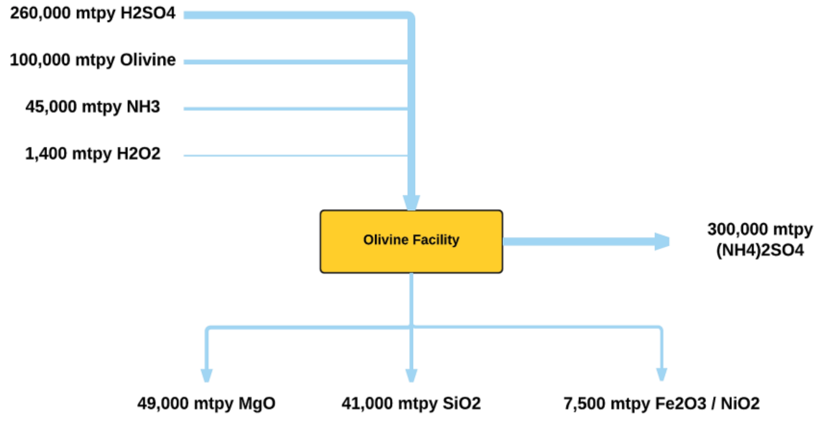
[$CaO + 2NH_4HSO_4 \rightarrow CaSO_4 + (NH_4)_2SO_4 + H_2O$]

Will NH_4HSO_4 attack olivine with appropriate recovery?

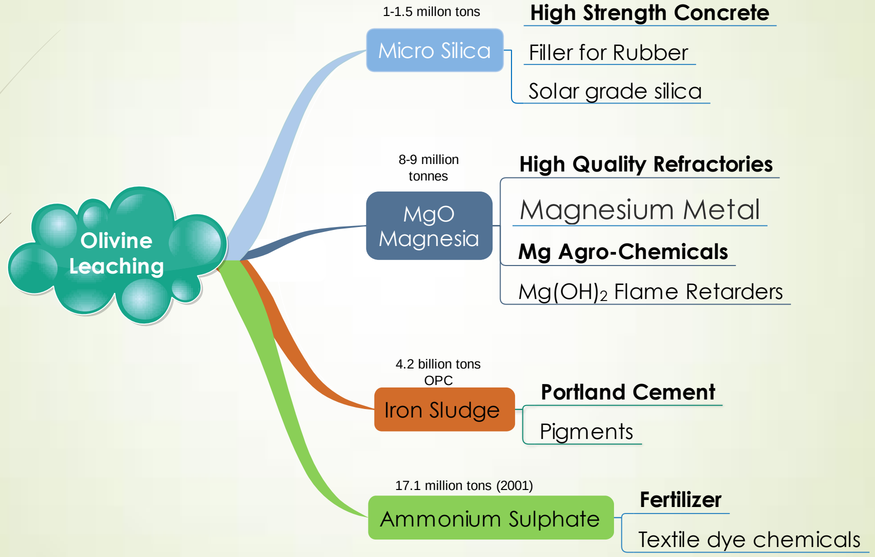
Primary Leach / Precipitation Circuit



Overall Mass Flows



Process Products



Economics with 5% of $(NH_4)_2SO_4$ Capacity Sold

5% of (NH4)2SO4 capacity sold, fixed loss see text						
Revenue		mtpy	$/ton	$/lb		$10^3/yr
	MgO	49,060	250			$ 12,265
	SiO2	41,110	384			$ 15,786
	Fe/Ni/O	7,458	for Ni	2		$ 0.57
	(NH4)2SO4*	10,129	300			$ 3,039
			Total			$ 31,091
Raw Materials		mtpy	$/ton	$/lb		$10^3/yr
	Olivine	100,000	35			$ 3,500
	NH3	2,236	$310			$ 693
	H2SO4	12,893	140			$ 1,805
	H2O2	1,360	1543.5			$ 2,099
			Total Raw Materials			$ 8,097
Energy		mtpy	$/ton			$10^3/yr
	H2O Evap	386,382	6.25			$ 2,415
	Decompositon of (NH4)2SO4**	331,386	100	kwh/ton		1,657
	Pumping solutions		1080619	kwh	$0.05	$54
	Heating Leaching Solns	813,089	$1			$ 813
	** Assumptn need data		Total Energy			$ 4,939
Labor		no per shift	avg $/wrk	shifts		
	Labor	10	80,000	4		3200
	Maintenance					3750
			Total Labor & Maint.			6950
	$10^3		Total Direct			19,986
Capital Costs	$	125,000	Indirect	40%	labor	1,280
Maint 3%	$	3,750.00	**Total Costs**			**21,266**
Payback yrs		13	Gross Profits			$ 9,825

Economics with 100% of $(NH_4)_2SO_4$ Capacity Sold

100%	of (NH4)2SO4 capacity sold, fixed loss see text					
Revenue		mtpy	$/ton	$/lb		$10^3/yr
	MgO	49,060	250			$ 12,265
	SiO2	41,110	384			$ 15,786
	Fe/Ni/O	7,458	for Ni	2		$ 0.57
	(NH4)2SO4*	297,583	300			$ 89,275
			Total			$ 117,327
Raw Materials		mtpy	$/ton	$/lb		$10^3/yr
	Olivine	100,000	35			$ 3,500
	NH3	44,730	$310			$ 13,866
	H2SO4	257,853	140			$ 36,099
	H2O2	1,360	1543.5			$ 2,099
			Total Raw Materials			$ 55,564
Energy		mtpy	$/ton			$10^3/yr
	H2O Evap	386,382	6.25			$ 2,415
	Decompositon of (NH4)2SO4**	-	100	kwh/ton		-
	Pumping solutions		1080619	kwh	$0.05	$54
	Heating Leaching Solns	813,089	$1			$ 813
	** Assumptn need data		Total Energy			$ 3,282
Labor		no per shift	avg $/wrk	shifts		
	Labor	10	80,000	4		3200
	Maintenance					3750
			Total Labor & Maint.			6950
	$10^3		Total Direct			65,796
Capital Costs	$ 125,000		Indireact	40%	labor	1,280
Maint 3%	$ 3,750.00		**Total Costs**			**67,076**
Payback yrs	2		Gross Profits			$ 50,250

Other Processing Options – H2SO4 & NH3

Pro's

- Simpler Flowsheet, no recycling of reagents
- Lower Capital Cost – less equipment
- Leaching recovery at same grind size may be higher

Cons

- No flexibility in output of $(NH_4)_2SO_4$, tied to MgO output

Unknown

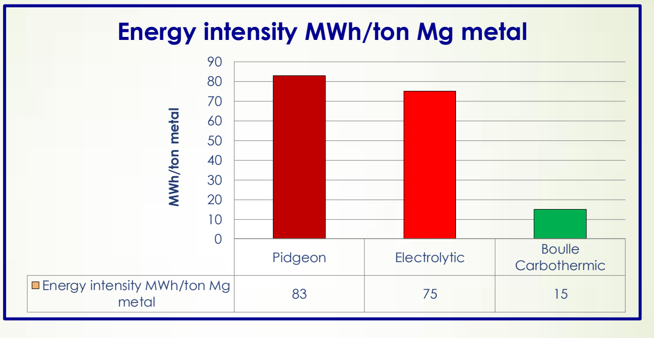
- Economics have not been evaluated, but expected to be slightly better than NH_4HSO_4

Summary of Options

Options for making MgO from Olivine include:

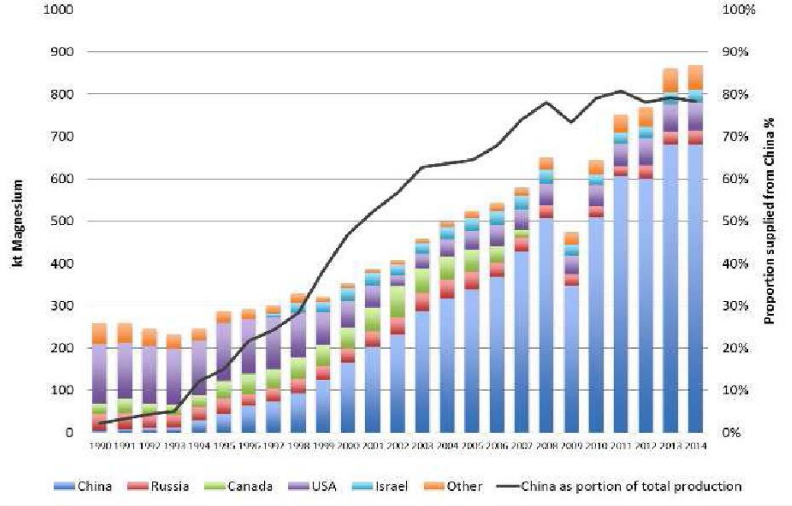
1. NH_4HSO_4 Process with production of micro-silica, iron oxide, MgO and as-sold amount of $(NH_4)_2SO_4$
   - Low cost
   - Allows flexibility in product mix
2. H_2SO_4 with NH_3 for with production of micro-silica, iron oxide, MgO, and $(NH_4)_4SO_4$
   - Need low cost supply of H_2SO_4
   - Must sell $(NH_4)_2SO_4$
   - Lowest capital costs.
3. H_2SO_4 and MgO with H_2SO_4 regeneration for production of micro-silica, iron oxide, MgO and $MgSO_4$.
   - Highest operating and capital cost
   - Need over the fence acid plant to make this option competitive

Carbothermic Mg Metal Production – Why?



Reference	GWP (kg CO2 -eq/kg Mg ingot)						
	AM process	Pidgeon, China	Carbothermic	Electrolytic	Magnetherm	Bolzano	Gossan- Zuliani
1	20.4- 26.4 (=24.3)	37-47 (=42)					
2		34 (+-8)	14 (+-8)	17 (+-8)			
3 and 4	27.9	43.3		16.1	17.6	13.8	9.1
5		25.3		14- 19; 6 if hydro		10.1	
6			13.5				

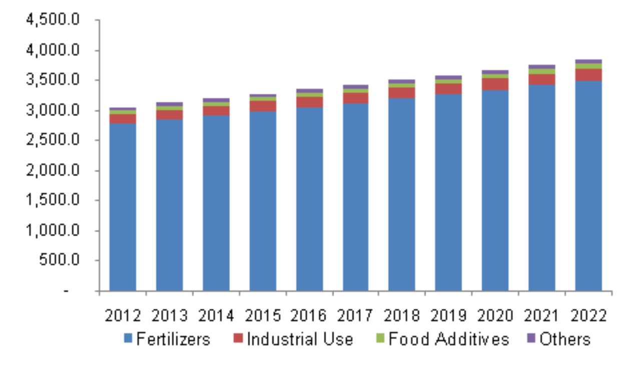
Global Mg Metal Production



Source: "The Economics of Magnesium Smelting Technology," John Grandfield, Light Metal Age, February 2016, pp60-65.

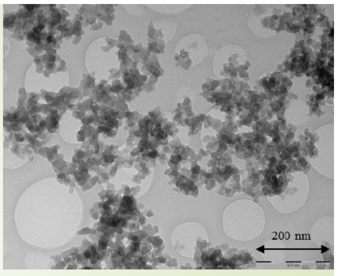
$(NH_4)_2SO_4$ Fertilizer

- Good on basic soils, high CaO soils
- $2.86 billion in sales and growing
- US Kilo Tons Ammonium Sulfate Production



Ref.: http://www.grandviewresearch.com/industry-analysis/ammonium-sulfate-market

Micro Silica (Fumes) notes



Silica Fume theoretical 1.5 million tons, less than 1 million tons used, limited growth, maybe 2 M tons theoretical in future

- Fly Ash availability > 700 million tons, increasing rapidly to?? (2000 million tons in 2020?)

- Other pozzolans:
- Mainly manufactured materials – limited by capacity
- GGBS (Ground granulated Blast Furnace Slag) 200 million tons?
- Limited increase – tied to steel production

Source: http://www.ibracon.org.br/eventos/50cbc/plenarias/PER_FIDJESTOL.pdf

Magnesia Recovery

Mg Precipitation
- Requires NH3 to raise pH and
- CO2 to make carbonate
  - MgCO3.Mg(OH)2.5H2O
- NH3 and CO2 Recycled
- Alternative with NH3 alone ??

MgCO3.Mg(OH)2.5H2O Decomposition
- >350 deg. C ?
- Liberates MgO, CO2, H2O

Iron Removed by raising pH with NH3

Iron Precipitation

- Oxidize any Ferrous iron to Ferric Iron
  - Ammonium Persulfate or
  - H_2O_2
  - ? Which more cost efficient?
- Raise pH with NH_3
  - $Fe^{+3} \rightarrow Fe(OH)_3$
  - Difficult to filter
  - Dry