

Testing required for the waste exclusion process Case study: Electrolytic Manganese Residue

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Creating strength.



Production Process

- Ore from Hotazel in the Northern Cape is beneficiated to Manganese Metal
- Also produce a dry manganese residue (filter cake) which is currently being landfilled



Annual EMM Sales by MMC

Manganese metal sales are increasingly being dominated by demand in the Green Electric Vehicle industry



Significant demand growth for high purity Manganese in the LIB segment

EV battery chemistry & high purity Mn-sulphate demand





High purity MnSO₄.H₂O demand in kt sulphate

Green customers want full life cycle accountability, including energy and landfilling

Source: RhoMotion Q4 2022 for CAM chemistry. Global MnSO₄ demand taken as the average of 4 different analyst groups (CRU, Roskill WM, Benchmark, Cairn Energy Research), updated Dec.2021. EU/NA portion as per MMC Feb.2022 estimates per each EU/NA-based pCAM maker/integrated battery maker with announced plans/intentions. EU/NA demand on this graph excludes Asian battery makers operating within EU/NA but consuming pCAMs made in Asia, e.g. LC Chem, CATL.

Construction of a 6000tpa Manganese Sulphate Plant in Mbombela

Purpose-built for the Electric Vehicle market, coming online Q2 2026



Residue Management Facility – Kingston Vale

Taken into operation in 2006, and operated under an ECA H:H permit, and a S74 Exemption



Zero Landfilling Future

MMC is actively seeking an alternative to landfilling of process residue:

- Gravity/Magnetic separation to produce a Mn-concentrate
 - Gravity separation was able to produce high concentrates, but yields were low
 - Magnetic separation tests still ongoing
- Chemically inerted fill material for construction / road building
 - High cost
- Roasting of residue to produce a general construction fill material plus sulphuric acid
 - Good results on the roasting, the residue becomes inert. But at a high cost?
 - Sulphuric acid production still pending
- Production of cement bricks
 - Great technical results! Commercials somewhat challenging.
- Production of clay bricks
 - Great technical results! Commercially more attractive.



Brick making methods

Cement Bricks

- Made from cement, sand and crushed aggregate
- Most important physical parameter is compressive strength (and friability)
- Most important chemical parameter is leachability
- Several variations tested varying the ratio's sand, cement and residue



- Waste Exclusion is viable mechanism
- But what testing is required for the rubber stamp?

Clay Bricks

- Made from clay, gravel and a small amount of coal
- Can be either open field kiln, or in a temperature controlled oven
- Most important physical parameter is compressive strength, but it has a SANS standard that governs other parameters
- Most important chemical parameter is leachability
- Clay brick "recipes" differ between the type of clay. So depending on the manufacturer, the amount of residue and firing temperature were varied



Atmospheric Emissions

According to individual and/or national legislation

SO₂ limits for field kilns and temperature controlled kilns



Radiello tubes positioned around a field kiln



Isokinetic sampling for T controlled kilns



Leachability

AS 4439.3-1997 Wastes sediments and contaminated soils - Preparation of leachates - Bottle leaching procedure

- Aggressive method to determine if nasties will leach out of a solid if in contact with an acidified water
- Based on landfill operations, so there is 1
 in 20 dilution
- Send the sample to an external laboratory, or...

Buy an Inductively Coupled Plasma Optical Emissions Spectrometer (ICP-OES)





Burnt clay masonry units

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• Shape

- Appearance
- Texture and colour
- Dimensions
- Warpage
- Compressive strength
- Efflorescence
- Soundness
- Water absorption

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Any reference to SABS 227 is deemed to be a reference to this standard (Government Notice No. 1373 of 8 November 2002)

SOUTH AFRICAN NATIONAL STANDARD

Burnt clay masonry units



Burnt clay masonry units



First you need to revamp your facilities...







Burnt clay masonry units

Get the basic equipment to make test samples



Mixer





Shape, Appearance, Texture and colour

Burnt clay masonry units

- Shape
 - No cavities, perforations etc.
- Appearance
 - Well burnt, no cracking etc.
- Texture and colour
 - Texture and colour should be uniform



Epic fail

Much nicer!



Burnt clay masonry units

- Dimensions
 - Tolerances specified in the standard
- Warpage
 - Limits for individual units and average of the set



1	2	3	4	5	6	7	
Class	Inc	dividual un mm	iits	Average dimensions of 32 units mm			
	Length	Width	Height	Length	Width	Height	
FBS	±7	±4	±4	± 3,5	±2	± 2	
FBX	±5	±3	± 3	± 2,5	± 1,5	± 1,5	
FBA	No	requireme	nt*	No requirement*			
NFP	No	o requireme	ent	± 3,5	± 2	±2	
NFX	No	o requireme	ent	± 3,5	±2	± 2	



Burnt clay masonry units

Compressive strength







Burnt clay masonry units

Efflorescence



Just a tray with water – and time





Burnt clay masonry units

Soundness



And then you check for pop-outs

"Steam cooker" and lime paint



Burnt clay masonry units

Water absorption, water soluble salts and moisture expansion



Crush and mix with DI water



Cook it down and measure what is left





Moisture expansion

Leachability



Leachates from bricks made in a temperature controlled kiln



SANS 227:2007

Start testing: small amount of waste, and remember the control!

				Control Mix (0%)		5% Larox Mix	
Test	Passing Criteria	Tests Conducted Per Mix	Pass Rate [%]	Average	Standard Deviation	Average	Standard Deviation
Dimensions (mm)	L ± 3.5; W ± 2; H ± 2 (Tolerance between 32 units)	32	100	L=105; W=46; H=24	L=0,768; W=0,274; H=0,328	L=105; W=46; H=23	L=2,152; W=0,540; H=0,473
Warpage (mm)	< 5	32	100	2.055	0.689	1.984	0.566
Compressive Strength (MPa)	NFP brick > 7; NFX brick > 14	12	100	17.215	2.124	34.696	6.284
Efflorescence (units)	10 units exhibiting slight efflorescence &10 units with moderate efflorescence.	20	100	0	N/A	2 (slight)	N/A
Soundness (pop outs)	Maximum 2 pop outs in 2/6 units	6	100	0	0	0	0
Water absorption (%)	8 – 20 (Cold)	6	100	14.584	0.542	10.919	0.498
Water- soluble salts (%)	< 0,1	6	100	-0.013	0.009	-0.051	0.054
Moisture expansion (%)	< 0,2	9	100	0.05	0.037	0.02	0.012



SANS 227:2007

Start testing: Larger amount of waste – all still good!

				Control Mix (0%)		10% Larox Mix	
Test	Passing Criteria	Tests Conducte d Per Mix	Pass Rate [%]	Average	Standard Deviation	Average	Standard Deviation
Dimensions (mm)	L ± 3.5; W ± 2; H ± 2 (Tolerance between 32 units)	32	100	L=105; W=46; H=24	L=0,768; W=0,274; H=0,328	L=105; W=46; H=23	L=1,570; W=0,180; H=0,228
Warpage (mm)	< 5	32	100	2.055	0.689	0.613	0.283
Compressive Strength (MPa)	NFP brick > 7; NFX brick > 14	12	100	17.215	2.124	15.738	1.251
Efflorescence (units)	10 units exhibiting slight efflorescence &10 units with moderate efflorescence.	20	100	0	N/A	4 (Slight)	N/A
Soundness (pop outs)	Maximum 2 pop outs in 2/6 units	6	100	0	0	0	0
Water absorption (%)	8 – 20 (Cold)	6	100	14.584	0.542	11.876	0.376
Water-soluble salts (%)	< 0,1	6	100	-0.013	0.009	-0.016	0.019
Moisture expansion (%)	< 0,2	9	100	0.05	0.037	0.04	0.033



SANS 227:2007

Continue testing: Keep the waste the same, but change the location

				Control Mix (0%)		10% Larox Mix	
Test	Passing Criteria	Tests Conducte d Per Mix	Pass Rate [%]	Average	Standard Deviation	Average	Standard Deviation
Dimensions (mm)	L ± 3.5; W ± 2; H ± 2 (Tolerance between 32 units)	32	100	L=113; W=42; H=21	L=1,250; W=0,491; H=0,174	L=113; W=42; H=21	L=1,023; W=0; H=0
Warpage (mm)	< 5	32	100	0.477	0.13	0.531	0.232
Compressive Strength (MPa)	FBS/FBX Brick > 24	12	100	84.303	7.695	86.571	9.072
Efflorescence (units)	At most, 10 units exhibiting slight efflorescence and 10 units with moderate efflorescence	20	100	12 (slight)	N/A	14 (slight)	N/A
Soundness (pop outs)	Maximum, 2 pop-outs in 2/6 units	6	100	0	0	0	0
Water absorption (%)	8 – 20 (Cold)	6	100	9.519	0.111	10.875	0.189
Water-soluble salts (%)	< 0,1	6	100	-0.008	0.005	-0.006	0.005
Moisture expansion (%)	< 0,2	9	100	0.01	0.009	0.04	0.02



SANS 227:2007

Continue testing: Keep the waste the same, but change the clay mix

				Control Mix (0%)		10% Larox Mix	
Test	Passing Criteria	Tests Conducte d Per Mix	Pass Rate [%]	Average	Standard Deviation	Average	Standard Deviation
Dimensions (mm)	L ± 3.5; W ± 2; H ± 2 (Tolerance between 32 units)	32	100	L=110; W=41; H=21	L=2,297; W=0; H=0	L=112; W=42; H=21	L=0,755; W=0; H=0
Warpage (mm)	< 5	32	100	0.484	0.124	0.469	0.083
Compressive Strength (MPa)	FBS/FBX Brick > 24	12	100	89.822	10.086	104.487	8.589
Efflorescence (units)	At most, 10 units exhibiting slight efflorescence and 10 units with moderate efflorescence	20	100	18 (slight)	N/A	8 (slight)	N/A
Soundness (pop outs)	Maximum, 2 pop-outs in 2/6 units	6	100	0	0	0	0
Water absorption (%)	8 – 20 (Cold)	6	100	11.239	0.215	10.631	0.112
Water-soluble salts (%)	< 0,1	6	100	-0.012	0.003	-0.006	0.003
Moisture expansion (%)	< 0,2	9	100	0.01	0.004	0.03	0.013



About 1000 tests later... all seems good!

Conclusions

Use of electrolytic manganese residue in clay bricks

- A waste exclusion provides a **potentially profitable** method of moving waste up the hierarchy, supported by **enabling legislation**
- From a company liability perspective (and from our very green clients!) due diligence is paramount
- So you have to test and develop the same quality procedures as with any of your normal products
- Invest in the right equipment and develop the skills necessary internally

Questions?

