Fingerprinting South African Cements

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1. Acknowledgement

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2. Abstract.

It is possible to identify CEM I cements, from South Africa, with a reasonable degree of certainty, using trace elements and some major elements. The characterization of blended cements can also be carried out using trace elements, but certain major elements may also be necessary to increase the level of certainty. The analysis of the constituent materials of the cement will simplify analysis and improve certainty. This is as a result of the limited number of cements produced and the unique raw materials found in the areas where the respective cement plants are situated in South Africa.

3. Introduction.

South Africa has four clinker producing cement manufacturers and numerous small cement manufacturers. The four major producers are Pretoria Portland Cement Company Limited (PPC), Lafarge South Africa, Holcim South Africa and Natal Portland Cement (a wholly owned subsidiary of Cimpor). The location of these plants is indicated in Appendix One.

With the adoption of the European Cement Specifications (EN 197 – 1 Composition, specifications and conformity criteria for common cements, EN 197 - 2: Conformity evaluation, and EN 413: Masonry Cement), in South Africa, certain of the major cement producers' cements (usually CEM I's) were being further blended by non clinker producing companies (using ground granulated slag and/or fly ash), resulting in cements with a high probability of poor performance. In anticipation of a need to identify the manufacturer of a cement or cement blends, the use of which may have resulted in construction problems, work has been done to assess whether it is possible to fingerprint the products manufactured by each clinker producing company.

In 2001, 2002 and 2004, campaigns were launched in South Africa, under the auspices of the Cement & Concrete Institute, whereby clinker, and associated materials of the major cement producers, were analysed with a view to assess if cements could be characterised by minor and/or trace elements. At this time CEM I's, CEM II's (A's and B's) and CEM III's (A's and B's) were being produced by the major manufacturers, with CEM II's, CEM III's, CEM V's and Masonry Cements being produced by the smaller blenders.

Under legislation at the time, certification of the respective cements was carried out by the South African Bureau of Standards.

4. Methods.

At the time, PPC had six clinker manufacturing plants where cement is produced and/or blended, spread throughout the country. Lafarge have one clinker manufacturing plant with one milling plant and one blending plant remote from the main manufacturing plant. Holcim have two clinker producing plants where cement is produced and/or blended, one milling plant and one blending plant, remote from the clinker plants.
Natal Portland Cement have one clinker manufacturing plant and two milling/blending plants, remote from the clinker plant.

In each of the campaigns, 2001 and 2002, for a 3 month period, cement, clinker, gypsum, slag (ground granulated slag or raw slag as the case might be), fly ash, limestone and, where appropriate, grinding additive, samples were collected. In 2004 only clinker was collected. These respective samples were composited and then reduced to approximately 1 kilogram each (1 litre in the case of grinding additives). In 2001 and 2002 these samples were submitted to the Cement and Concrete Institute, where they were coded prior to submission to an independent laboratory.

The selection of an independent laboratory was based on the submission of some certified reference clinkers and cements to a number of laboratories and selecting the laboratory with the best fit of results. X – Ray Fluorescence Spectroscopy and Inductively Coupled Plasma techniques were specified as the medium for analysis. Methods of analysis were left to individual laboratories. The laboratory selected was Anglo American Research Laboratory (AARL), the main research laboratory for Anglo American PLC. In

2004 the individual manufacturers submitted their respective samples individually to AARL.

With the trace elements available from the cement input materials and the cement itself, it was possible for the individual manufacturers (who know their respective cement composition) to cross check the accuracy of the analyses.

The following trace elements were analysed
V, Cr, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr,Y, Zr, Nb, Mo, Ag, Cd In, Sn, Sb, Te, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Ir, Pt, Au, Hg, Tl, Pb, Bi, Th, U, along with Mg, Ti, Mn.
Only Sr, Ba, Zr, Mn and Ti were used in the primary analysis, while some of the major elements were considered where necessary (MgO for example).

5. Results and Discussion.

While Anglo American Research Laboratories conducted the trace element analyses, producer companies analysed the cements and clinkers themselves for the usual elemental analyses. The raw materials used by these plants differentiates some plants e.g. Plant E which has a high Mn_2O_3 level – usually a factor of 2 higher than the next closest Plant.
As such it is easy to recognize when in a CEM I cement. Some plants have unique alkali and/or MgO levels when compared to others. Once again, easy markers for fingerprinting.

Although not conducted in this exercise, a good practice would be to analyse the cement for it's constituent materials as indicated in EN 196 – 4:2000, Part 4: Quantitative determination of constituents. These constituents are referred to as "extenders" i.e. ground granulated blastfurnace slag, fly ash and limestone.

Slag is sourced from four sources. Plant C uses the entire arisings from one of the sources, leaving three sources for use by the rest of the Industry. One source is geographically isolated to a specific part of South Africa and as such when used for blended cements, only two cement plants are likely to make use of it.

Fly ash is sourced from 4 power stations, three of which are from the national electricity producer ESKOM. The other source is from a municipal power station.

The analysis assumes that a sample of the cement is available.

Initial analysis was done using CEM I and CEM II cements. The decision tree (Appendix Three) was based on the following;

- Take the Strontium, Barium, Zirconium, Titanium results in ppm
- Sum the Strontium, Barium and Zirconium
- Express these elements as a percentage of this sum
- Determine the Sr/Zr and Sr/Ba ratios based on these percentages
- Determine the Ti/Sr ratio based on the ppm results.

These results are reflected in the table in Appendix Two.

The impact of the extenders can be seen when we look at the typical levels of extenders available – see table below.

Extender's selected trace elements

Year	Origin	Product	Method	Sr	Ti	Ba	Zr	Cr	Mn
2001	Source A	Fly Ash	ICP MS	915	10909	1198	455	258	465
2001	Source A	Fly Ash	ICP MS	922	10789	1240	457	270	465
2002	Source A	Fly Ash	XRF	923	10490	1156	471	306	235
2001	Source B	Fly Ash	ICP MS	1441	10969	1697	536	189	465
2001	Source B	Fly Ash	ICP MS	2724	11329	2382	536	189	774
2002	Source B	Fly Ash	XRF	1802	10729	1845	517	229	235
2002	Source B	Fly Ash	XRF	2465	10789	2135	502	226	235
2004	Source C	Fly Ash	ICP MS	473		420	2	30	
2001	Source A	Slag	ICP MS	779	4196	1054	446	49	12698
2002	Source A	Slag	XRF	868	3896	939	392	137	6665
2004	Source B	Slag	ICP MS	1396		676	7	14	
2001	Source C	Slag	ICP MS	53	2577	74	24	28845	4026

One notices that the XRF and Inductively Coupled Plasma results are different for the same material, with ICP giving slightly higher results.

Slag

The Source C slag, originating from a ferro-chrome source, is characterised by significant chrome levels. Extension with this slag will elevate chrome levels to amounts way above the norm for South African cements, which are usually below 200 ppm. The levels of Strontium, Barium and Zirconium are correspondingly very low. As such the use of this slag will be immediately obvious from the chrome levels and the quantity of elements used to differentiate the purer cements will not affect their differentiation.

The Source B slag is only likely to be used with Plants H and A cements, due to geographical location of the slag. At 50% extension, Sr levels will be lowered somewhat, but the Sr levels in this slag are also elevated as it is derived from limestone and dolomites from a similar geographic region. The decision rules derived above would thus still hold.

Slag Source A is characterised by levels of Ba, Mn and Ti not seen in conventional CEM I's. Identification of Plant G & D could be affected by these levels. Extension of greater than 30% with a Plant D CEM I, will still characterise Plant D according to the rules reflected above. Use with Plant G is unlikely due to geographic location, but should it occur the Sr/Ba ratio will be lowered below 4 and one would still characterise Plant G as all the other cements would also have lowered Sr/Ba ratios.

So it will still be able to identify cements with these slags, using the decision tree in Appendix Three.

Fly Ash.

The source of the coals used in the power stations yielding fly ash come from the same geographic area and are characterised as the Witbank coalfields. These coals are of similar rank and the ash constituents appear to be similar when considering Ti levels, which are factors of 5 greater than that found in typical CEM I's from South Africa. These ashes are also mildly radioactive as a result of normally occurring radioactive materials (NORM), with activity levels below 200 Becquerel's per kilogram. This is consistent with most fly ashes found throughout the world.

Examining the Ti levels of any of the CEM I's and finding levels in excess of 4 500 ppm will indicate that fly ash has been used as an extender.

In Appendix Four we have a decision tree for Blends (Fly ash) which is similar to that for CEM I's, but there is a difference when identifying Plant G when looking at the Sr/Ba ratio of the blended cements. Also the decision between Plants F and J are reversed compared to CEM I when looking at the Zr content.

It must also be said that there is an increased level of uncertainty when looking at Fly Ash blends and secondary investigation could be necessary to identify the host cement.

When considering CEM V cements, one has both Fly Ash and Slag present. Elevated Ti levels will indicate the presence of Fly Ash. The levels are likely to be below 4 500 ppm, but greater than 3 000 ppm (since Fly ash content is likely to be between 15 and 25%). As indicated earlier elevated Cr levels will identify the slag source. To identify the source of the clinker, one would need to use the results from the constituent analysis (% slag, % fly ash etc) as indicated above. This will enable one to remove the Sr, Ba and Zr (assuming an average slag and an average fly ash). This will enable one to analyse as per the decision tree in Appendix Three.

Limestone.

Limestone extension is usually only carried out at the sites from which the clinker is produced. This being the case, the trace and/or minor elements are simply lower that what one would find in the cement, as the limestone has not been calcined and still contains the carbon dioxide. The impact of this will be dilution of all the elements in question. However, respective relative percentages and ratios will be unaffected and characterization of host Plant will be possible

The use of limestone is largely academic since limestone is not sold commercially and cements produced containing limestone are not usually used as a base for further extension.

6. Conclusions

Using Strontium, Barium, Zircon, Titanium, Managanese and Chrome, it is possible to characterise CEM I cements with a reasonable degree of certainty. This certainty is governed by the accuracy of the test results and consistency of these elements in the cements. Only two periods were examined for this paper, but subsequent work on clinkers by individual companies has indicated some measure of consistency – within the vagaries of nature.

In identifying cements blended with Slag, one has to increase the number of trace elements, firstly to identify if a slag is present (Manganese and Barium will usually do this) and secondly to differentiate the slags (chrome does this). The rule used for CEM I characterization will suffice.

In identifying cements blended with Fly Ash, there is an element of uncertainty in using the same rules, albeit with different sets of values for the decision tree identified for CEM I cements. The Titanium levels of South African Fly Ashes have significant levels of

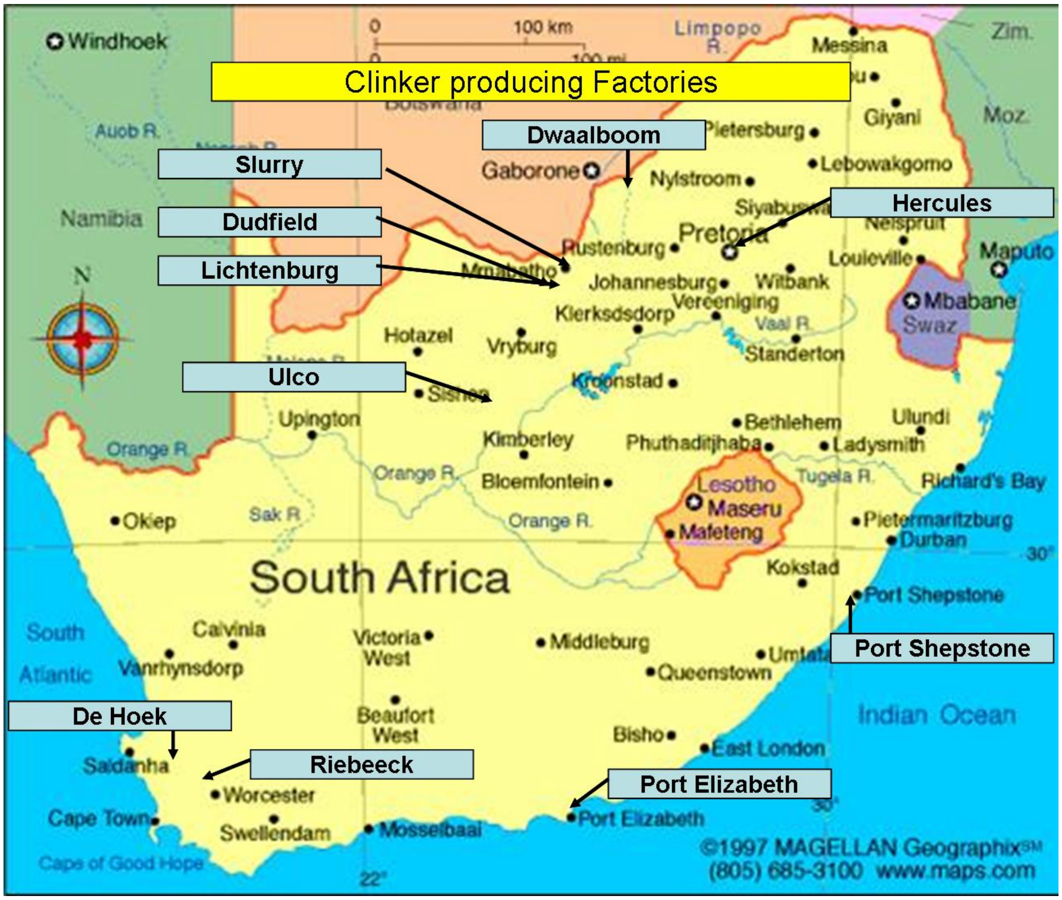
Titanium when compared to the CEM I's. However, there seems to sufficient evidence to suggest that identification could be done with adequate accuracy.

The level of certainty can be increased by determining the percentage of constituent materials (% slag, % fly ash etc), enabling one to "strip out" the Sr, Zr and Ba arising from slag and fly ash. This will enable identification of the host clinker using the method mentioned above.

7. References

[1] Ference D Tamas and Janos Abnonyi. WORLD MAP OF CLINKERS – VISULATION OF TRACE ELEMENT CONTENT OF CLINKERS BY SELF-ORGANIZING MAP. Proceedings of the 11th International Conference on the Chemistry of Cement (2003).
[2] J H Potgieter. Fingerprinting S.A. Cements by chemical analysis. In: H. Justnes (Ed). Proceeedings of the 10th International Conference on the Chemistry of Cement (1997).

Appendix One.



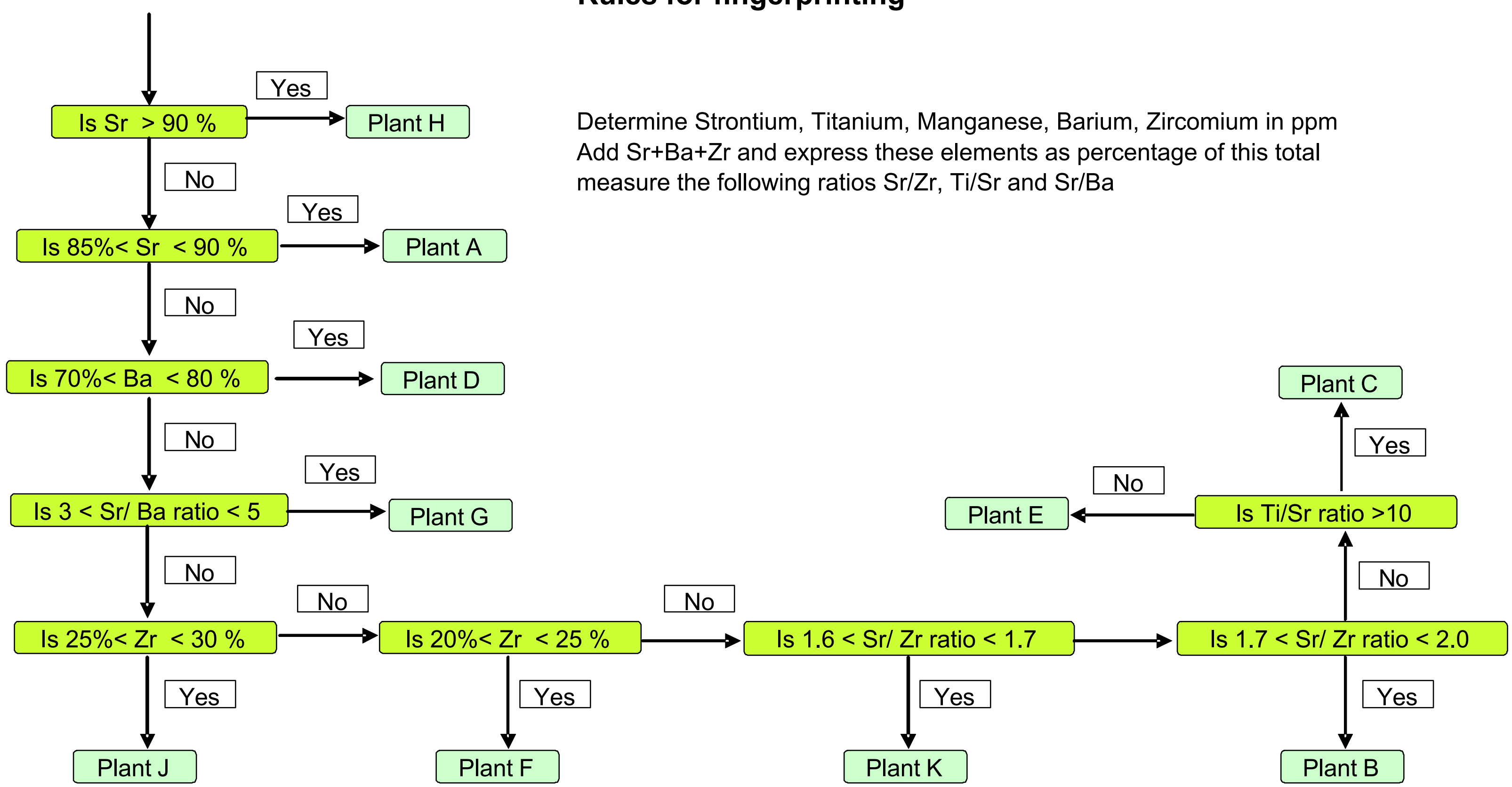
Appendix Two – Analysis results ppm

Plant	Cement	Year	Method	Sr	Ti	Ba	Zr	Sum	Sr	Ba	Zr	Sr/Zr	Sr/Ba	Ti/Sr
Plant H	CEM I	2001	ICP MS	2420	1199	158	82	2660	91.0%	5.9%	3.1%	29.40	15.29	0.50
Plant A	CEM II	2002	XRF	3042	1499	201	136	3379	90.0%	6.0%	4.0%	22.34	15.10	0.49
Plant A	CEM II	2001	ICP MS	2733	1558	329	145	3207	85.2%	10.3%	4.5%	18.90	8.30	0.57
Plant D	CEM I	2001	ICP MS	67	1678	567	80	714	9.4%	79.4%	11.2%	0.84	0.12	24.98
Plant D	CEM I	2001	ICP MS	67	1948	568	89	724	9.3%	78.4%	12.3%	0.75	0.12	28.91
Plant D	CEM I	2002	XRF	88	1379	549	75	711	12.3%	77.1%	10.5%	1.17	0.16	15.69
Plant D	CEM I	2002	XRF	109	1618	607	77	792	13.8%	76.6%	9.7%	1.42	0.18	14.84
Plant D	CEM II	2001	ICP MS	99	1918	596	88	783	12.6%	76.1%	11.3%	1.12	0.17	19.43
Plant G	CEM II	2002	XRF	680	2038	146	486	1312	51.8%	11.1%	37.0%	1.40	4.66	3.00
Plant G	CEM II	2001	ICP MS	716	1678	218	382	1315	54.4%	16.5%	29.0%	1.88	3.29	2.34
Plant J	Clinker	2002	XRF	75	1918	204	116	394	18.9%	51.7%	29.4%	0.64	0.37	25.70
Plant J	Clinker	2001	ICP MS	82	1499	222	122	426	19.3%	52.0%	28.6%	0.67	0.37	18.20
Plant F	CEM I	2002	XRF	178	1978	366	165	710	25.1%	51.6%	23.3%	1.08	0.49	11.09
Plant F	CEM I	2001	ICP MS	189	2098	375	168	731	25.8%	51.3%	22.9%	1.12	0.50	11.13
Plant F	CEM II	2002	XRF	178	2278	391	168	737	24.1%	53.1%	22.8%	1.06	0.45	12.83
Plant F	CEM I	2002	XRF	257	2338	366	183	806	31.9%	45.4%	22.7%	1.40	0.70	9.11
Plant F	CEM II	2001	ICP MS	188	2038	302	136	627	30.0%	48.2%	21.8%	1.38	0.62	10.84
Plant F	CEM I	2001	ICP MS	254	2398	394	176	824	30.9%	47.7%	21.4%	1.44	0.65	9.43
Plant K	OPC	2002	XRF	218	2398	281	136	635	34.4%	44.3%	21.4%	1.61	0.78	10.98
Plant B	CEM I	2002	XRF	167	1319	208	94	468	35.6%	44.5%	20.0%	1.78	0.80	7.91
Plant B	CEM I	2001	ICP MS	278	2098	242	137	656	42.3%	36.8%	20.9%	2.03	1.15	7.56
Plant C	CEM I	2002	XRF	236	2997	163	80	479	49.3%	34.0%	16.6%	2.97	1.45	12.68
Plant C	CEM I	2001	ICP MS	208	1918	166	66	440	47.2%	37.7%	15.1%	3.14	1.25	9.23
Plant C	CEM I	2002	XRF	345	4256	281	115	740	46.6%	37.9%	15.5%	3.00	1.23	12.34
Plant C	CEM I	2001	ICP MS	324	3237	329	121	774	41.8%	42.5%	15.7%	2.67	0.98	10.00
Plant C	CEM II	2002	XRF	452	5395	353	170	975	46.3%	36.3%	17.4%	2.66	1.28	11.94
Plant C	CEM II	2001	ICP MS	576	5634	743	243	1562	36.9%	47.6%	15.6%	2.37	0.77	9.79
Plant C	CEM III	2002	XRF	599	6953	469	232	1301	46.0%	36.1%	17.9%	2.58	1.28	11.61
Plant C	CEM III	2001	ICP MS	418	4076	485	162	1065	39.2%	45.6%	15.2%	2.58	0.86	9.76
Plant E	CEM I	2002	XRF	217	1499	148	66	431	50.5%	34.2%	15.3%	3.30	1.47	6.90
Plant E	CEM I	2002	XRF	222	1259	186	67	476	46.7%	39.1%	14.2%	3.30	1.20	5.66
Plant E	CEM I	2001	ICP MS	200	1439	201	84	486	41.3%	41.4%	17.3%	2.38	1.00	7.18
Plant E	CEM I	2001	ICP MS	223	1618	219	85	527	42.4%	41.5%	16.1%	2.63	1.02	7.24
Plant E	CEM II	2002	XRF	437	2937	498	129	1063	41.1%	46.8%	12.1%	3.39	0.88	6.73
Plant E	CEM II	2002	XRF	558	4615	769	181	1507	37.0%	51.0%	12.0%	3.09	0.73	8.27
Plant E	CEM II	2001	ICP MS	495	5095	874	211	1580	31.3%	55.3%	13.4%	2.34	0.57	10.29
Plant E	CEM II	2001	ICP MS	366	4016	728	174	1268	28.9%	57.4%	13.7%	2.10	0.50	10.97

Appendix Three

Rules for fingerprinting

Determine Strontium, Titanium, Manganese, Barium, Zircomium in ppm
Add Sr+Ba+Zr and express these elements as percentage of this total
measure the following ratios Sr/Zr, Ti/Sr and Sr/Ba



Appendix Four

Rules for fingerprinting fly ash blends

Determine Strontium, Titanium, Manganese, Barium, Zircomium in ppm
Add Sr+Ba+Zr and express these elements as percentage of this total
measure the following ratios Sr/Zr, Ti/Sr and Sr/Ba