

Table 6.3: Limestone neutralisation reaction data and % solid and water content results

Limestone, mass (g)	12.50
AMD, volume (ml)	500
Neutralisation Reaction , speed (rpm)	250
time (min)	pH
0	2.81
60	5.79
121	5.92
180	6.07
240	6.06
300	6.08
360	6.07
360	settling
470	separation of liquid and solids
Process water, volume (ml)	380
Residual solids, wet mass (g)	124.67
Dried at 105 °C for over 12 hr	
Dry mass (g)	15.23
Water content (%)	87.8
Solid content (%)	12.2

Table 6.4: Acidity and sulphate concentration of treated AMD from the limestone neutralisation reaction

Acidity of process water			
Process water, volume (ml)	10	Process water, volume (ml)	10
Process water diluted, volume (ml)	100	Process water diluted, volume (ml)	100
0.1 N NaOH, normality (N)	0.1015	0.1 N NaOH, normality (N)	0.1015
Titration volume of NaOH solution (ml)	pH	Titration volume of NaOH solution (ml)	pH
	0		0
	4.90		5.06
	10.1		8.30
	8.30		10.05
Acidity (meq/l)	102.3		
Molar mass of CaCO ₃ (g/mol)	100.09		
Acidity (mg/l CaCO₃)	5118		
Sulphate, SO₄²⁻ (mg/l)	9680		

The data and results of the Arnot fly ash neutralisation reactions at 1:7 ratio, as well as the % solids and % water content are presented in Table 6.5. The results are presented as detailed above for the limestone neutralisation reaction. The acidity and sulphate concentration of the treated AMD, termed process water, from the Arnot fly ash neutralisation reaction is listed in Table 6.6. The results are presented as detailed for the limestone neutralisation reaction.

Table 6.5: Arnot fly ash neutralisation reaction data and % solid and water content results (1:7 ratio)

Fly ash, mass (g)	71.43
AMD, volume (ml)	500
Neutralisation Reaction , speed (rpm)	250
time (min)	pH
0	2.74
80	5.33
120	5.30
182	5.51
300	5.36
300	settling
358	separation of liquid and solids
Process water, volume (ml)	380
Residual solids, wet mass (g)	179.22
Dried at 105 °C for over 12 hr	
Dry mass (g)	77.77
Water content (%)	56.6
Solid content (%)	43.4

Table 6.6: Acidity and sulphate concentration of treated AMD from the Arnot fly ash neutralisation reaction (1:7 ratio)

Acidity of process water			
Process water, volume (ml)	10	Process water, volume (ml)	10
Process water diluted, volume (ml)	100	Process water diluted, volume (ml)	100
0.1 N NaOH, normality (N)	0.1015	0.1 N NaOH, normality (N)	0.1015
Titration volume of NaOH solution (ml)	pH	Titration volume of NaOH solution (ml)	pH
0	5.15	0	4.97
13.95	8.30	14.0	8.30
Acidity (meq/l)	141.8		
Molar mass of CaCO ₃ (g/mol)	100.09		
Acidity (mg/l CaCO₃)	7099		
Sulphate, SO₄²⁻ (mg/l)	W12720		

The data and results of the Arnot fly ash neutralisation reactions at 1:4 ratio, as well as the % solids and % water content are presented in Table 6.7. The acidity and sulphate concentration of the treated AMD, termed process water, is listed in Table 6.8. The data and results are presented as detailed for the Arnot fly 1:4 ratio neutralisation reaction.

Table 6.7: Arnot fly ash neutralisation reaction data and % solid and water content results (1:4 ratio)

Fly ash, mass (g)		125.00
AMD, volume (ml)		500
Neutralisation Reaction , speed (rpm)		250
	time (min)	pH
	0	2.74
	80	5.78
	120	5.87
	180	5.94
	300	5.93
	300	settling
	363	separation of liquid and solids
Process water, volume (ml)		320
Residual solids, wet mass (g)		299.23
Dried at 105 °C for over 12 hr		
Dry mass (g)		134.45
Water content (%)		55.1
Solid content (%)		44.9

Table 6.8: Acidity and sulphate concentration of treated AMD from the Arnot fly ash neutralisation reaction (1:4 ratio)

Acidity of process water			
Process water, volume (ml)	10	Process water, volume (ml)	10
Process water diluted, volume (ml)	100	Process water diluted, volume (ml)	100
0.1 N NaOH, normality (N)	0.1015	0.1 N NaOH, normality (N)	0.1015
Titration volume of NaOH solution (ml)	pH	Titration volume of NaOH solution (ml)	pH
	0	0	5.38
	17.0	8.55	8.30
Acidity (meq/l)	86.5		
Molar mass of CaCO ₃ (g/mol)	100.09		
Acidity (mg/l CaCO ₃)	4330		
Sulphate, SO ₄ ²⁻ (mg/l)	9530		

The data and results of the Hendrina fly ash neutralisation reactions at 1:7 ratio, as well as the % solids and % water content are presented in Table 6.9. The acidity and sulphate concentration of the treated AMD, termed process water, is listed in Table 6.10. The data and results are presented as detailed for the Arnot fly neutralisation reaction.

Table 6.9: Hendrina fly ash neutralisation reaction data and % solid and water content results (1:7 ratio)

Fly ash, mass (g)		71.43
AMD, volume (ml)		500
Neutralisation Reaction , speed (rpm)		250
	time (min)	pH
	0	2.83
	60	5.93
	120	5.78
	180	5.53
	240	5.43
	300	5.35
	362	5.26
	362	settling
	425	separation of liquid and solids
Process water, volume (ml)		390
Residual solids, wet mass (g)		173.00
Dried at 105 °C for over 12 hr		
Dry mass (g)		72.66
Water content (%)		58.0
Solid content (%)		42.0

Table 6.10: Acidity and sulphate concentration of treated AMD from the Hendrina fly ash neutralisation reaction (1:7 ratio)

Acidity of process water			
Process water, volume (ml)	10	Process water, volume (ml)	10
Process water diluted, volume (ml)	100	Process water diluted, volume (ml)	100
0.1 N NaOH, normality (N)	0.1015	0.1 N NaOH, normality (N)	0.1015
Titration volume of NaOH solution (ml)	pH	Titration volume of NaOH solution (ml)	pH
0	4.86	0	5.08
13.50	8.30	13.60	8.30
Acidity (meq/l)	137.5		
Molar mass of CaCO ₃ (g/mol)	100.09		
Acidity (mg/l CaCO₃)	6883		
Sulphate, SO₄²⁻ (mg/l)	11560		

Hendrina fly ash neutralisation reaction data and results at 1:4 ratio are presented in Table 6.11 and 6.12. The data and results are presented as for the previous experiments. Table 6.11 tabulates the neutralisation reaction data and % solid and water content. Table 6.12 tabulates the acidity determination data and results and sulphate content of the process water.

Table 6.11: Hendrina fly ash neutralisation reaction data and % solid and water content results (1:4 ratio)

Fly ash, mass (g)		125.00
AMD, volume (ml)		500
Neutralisation Reaction , speed (rpm)		250
	time (min)	pH
	0	2.80
	60	6.03
	120	5.94
	182	5.84
	240	5.76
	300	5.66
	360	5.51
	360	settling
	415	separation of liquid and solids
Process water, volume (ml)		325
Residual solids, wet mass (g)		287.09
Dried at 105 °C for over 12 hr		
Dry mass (g)		125.50
Water content (%)		56.3
Solid content (%)		43.7

Table 6.12: Acidity and sulphate concentration of treated AMD from the Hendrina fly ash neutralisation reaction (1:4 ratio)

Acidity of process water			
Process water, volume (ml)	10	Process water, volume (ml)	10
Process water diluted, volume (ml)	100	Process water diluted, volume (ml)	100
0.1 N NaOH, normality (N)	0.1015	0.1 N NaOH, normality (N)	0.1015
Titration volume of NaOH solution (ml)	pH	Titration volume of NaOH solution (ml)	pH
0	5.25	0	5.08
6.1	8.30	Sample split and discarded	
Acidity (meq/l)	61.4		
Molar mass of CaCO ₃ (g/mol)	100.09		
Acidity (mg/l CaCO₃)	3073		
Sulphate, SO₄²⁻ (mg/l)	7910		

Kriel fly ash neutralisation reaction data and results at 1:7 ratio are presented in Table 6.13 and 6.14. The data and results are presented as for the previous experiments. Table 6.13 tabulates the neutralisation reaction data and % solid and water content. Table 6.14 tabulates the acidity determination data and results and sulphate content of the process water.

Table 6.13: Kriel fly ash neutralisation reaction data and % solid and water content results (1:7 ratio)

Fly ash, mass (g)	71.43
AMD, volume (ml)	500
Neutralisation Reaction , speed (rpm)	250
time (min)	pH
0	2.70
67	5.73
160	5.49
210	5.74
280	5.42
280	settling
330	separation of liquid and solids
Process water, volume (ml)	385
Residual solids, wet mass (g)	176.89
Dried at 105 °C for over 12 hr	
Dry mass (g)	79.29
Water content (%)	55.2
Solid content (%)	44.8

Table 6.14: Acidity and sulphate concentration of treated AMD from the Kriel fly ash neutralisation reaction (1:7 ratio)

Acidity of process water			
Process water, volume (ml)	10	Process water, volume (ml)	10
Process water diluted, volume (ml)	100	Process water diluted, volume (ml)	100
0.1 N NaOH, normality (N)	0.1015	0.1 N NaOH, normality (N)	0.1015
Titration volume of NaOH solution (ml)	pH	Titration volume of NaOH solution (ml)	pH
	0		0
	11.7		21.5
Acidity (meq/l)	113.9		
Molar mass of CaCO ₃ (g/mol)	100.09		
Acidity (mg/l CaCO₃)	5702		
Sulphate, SO₄²⁻ (mg/l)	9850		

Kriel fly ash neutralisation reaction data and results at 1:4 ratio are presented in Table 6.15 and 6.16. The data and results are presented as for the previous experiments. Table 6.15 tabulates the neutralisation reaction data and % solid and water content. Table 6.16 tabulates the acidity determination data and results and sulphate content of the process water.

Table 6.15: Kriel fly ash neutralisation reaction data and % solid and water content results (1:4 ratio)

Fly ash, mass (g)	125.00
AMD, volume (ml)	500
Neutralisation Reaction , speed (rpm)	250
time (min)	pH
0	2.67
67	6.31
160	6.19
210	6.35
280	6.45
280	settling
340	separation of liquid and solids
Process water, volume (ml)	315
Residual solids, wet mass (g)	308.18
Dried at 105 °C for over 12 hr	
Dry mass (g)	139.64
Water content (%)	54.7
Solid content (%)	45.3

Table 6.16: Acidity and sulphate concentration of treated AMD from the Kriel fly ash neutralisation reaction (1:4 ratio)

Acidity of process water			
Process water, volume (ml)	10	Process water, volume (ml)	10
Process water diluted, volume (ml)	100	Process water diluted, volume (ml)	100
0.1 N NaOH, normality (N)	0.1015	0.1 N NaOH, normality (N)	0.1015
Titration volume of NaOH solution (ml)	pH	Titration volume of NaOH solution (ml)	pH
	0		0
	4.0		3.65
Acidity (meq/l)	37.0		
Molar mass of CaCO ₃ (g/mol)	100.09		
Acidity (mg/l CaCO ₃)	1854		
Sulphate, SO ₄ ²⁻ (mg/l)	5820		

6.3.2 Discussion of results obtained for the comparison of limestone versus fly ash neutralisation of Toeseep AMD

All the data and results obtained from the neutralisations experiments in **Section 6.5.2** are tabulated in Table 6.17. This allowed a detailed comparison of process conditions and results from the neutralisation of AMD with limestone and various fly ashes. The individual experiments are allocated test numbers in Table 6.17

Table 6.17: Comparison of result for limestone and fly ash treatments of high sulphate Toeseep AMD

NOTE: This cost comparison does not consider the additional costs of the biological process needed after limestone treatment

	Test number	1	2	3	4	5	6	7
AMD	pH	2.81	2.74	2.74	2.83	2.80	2.70	2.67
water quality	Acidity (mg/l as CaCO ₃)	12 291	12 291	12 291	12 291	12 291	12 291	12 291
	Sulphate concentration (mg/l)	17 100	17 100	17 100	17 100	17 100	17 100	17 100
Neutralisation	Neutralising material	Limestone	Arnot FA	Arnot FA	Hendrina FA	Hendrina FA	Kriel FA	Kriel FA
	Alkalinity (% as CaCO ₃)	98	13	13	13	13	18	18
	Reaction time (hours)	6.0	5.0	5.0	6.0	6.0	4.7	4.7
Material usage	(kg/m ³ of AMD)	25	143	250	143	250	143	250
Recovered water	pH	6.1	5.4	5.9	5.3	5.5	5.4	6.4
	Acidity (mg/l as CaCO ₃)	5 118	7 099	4 330	6 883	3 073	5 702	1 854
	Sulphate concentration (mg/l)	9 680	12 720	9 530	11 560	7910	9 850	5 820
Residual sludge	Settling time (hours)	1.8	1.0	1.1	1.1	0.9	0.8	1.0
	Mass recovered (kg/kg material used)	10	2.5	2.4	2.4	2.3	2.5	2.5
	Solid content (%)	12	43	45	42	44	45	45

	Test number	1	2	3	4	5	6	7
Costs	Neutralising material price (R/t)	97.60	0	0	0	0	0	0
	Flocculant cost (R/kg sludge)	0.0007	0	0	0	0	0	0
	Neutralisation cost (R/m ³ of AMD) excluding transport	2.62	0	0	0	0	0	0
	Transport cost (R/t)	72.40	55	55	55	55	55	55
	Neutralisation cost (R/m ³ of AMD) including transport	4.28	7.86	13.75	7.86	13.75	7.86	13.75
	Acidity removal cost (R/kg as CaCO ₃) including transport	0.62	1.51	1.73	1.45	1.49	1.19	1.32
	Sulphate removal cost (R/kg) including transport	0.60	1.79	1.82	1.42	1.50	1.08	1.22



In the case of fly ash (Table 6.17), a larger mass was used because of the lower CaCO_3 content (13-18 % CaCO_3 for fly ash versus 98 % for limestone) (Table 6.17) of fly ash for treatment of the contaminated AMD tested (Table 6.17). Less fly ash was needed for treatment of the Skoongesig AMD, which contained lesser sulphate concentrations, than the Toeseep AMD (**Chapter 5**). This simulation used only enough fly ash to bring water to a comparable pH as could be achieved with limestone. A pH of about 7.5 is the maximum that can be attained using limestone, whereas fly ash can increase the pH to higher levels as required, depending on the quantity used and the contact time. The AMD was neutralised in 6 hours with limestone whilst the fly achieved neutralisation in 5 hours. The residual acidity and sulphate loads are still high in all cases at the pH attained for both limestone and fly ash. The sulphate, TDS and toxic element content could be further reduced by achieving a higher pH with fly ash either using a longer contact time or more ash.

A limestone dosage of 25 kg/m^3 (Table 6.17: test 1) led to a similar decrease in acidity and sulphate load compared to fly ash at higher dosages of 143 kg/m^3 for Kriel fly ash (Table 6.17: test 6), 250 kg/m^3 for Hendrina and Arnot fly ash (Table 6.17: tests 3, 5). Kriel fly ash at 250 kg/m^3 (Table 6.17: test 7) allowed for a more significant decrease in acidity and sulphate load, because of its higher alkalinity. Higher fly ash dosages would achieve complete neutralisation of AMD, but may not be applicable in the current primary liming plant as the limits of pump ability of the sludge may be reached, due to high solid contents.

Acidity expressed as mg/l as CaCO_3 , was reduced from 12291 mg/l to 1850 mg/l when using Kriel fly ash over 4.7 hours (Table 6.1: test 7) at a dosage of 250 kg/m^3 of AMD compared to limestone, in which case the acidity was only reduced to 5120 mg/l as CaCO_3 over 6 hours. The kg/m^3 of AMD dosage used for limestone was however lower. The simulation shows that limestone is somewhat efficient as neutralising agent but does not achieve high sulphate removal from AMD.

In the simulated study a reduction of about 40 % of the usual efficiency of neutralisation was observed in the case of limestone, compared to that currently achieved on a full scale plant (Maree *et al.* 2004). This loss of efficiency was likely

caused by the conditions applied in the simulated study. It is expected that the results of the simulation given here using fly ash show a similar reduction in efficiency. Thus the fly ash neutralisation capacity can be expected to increase proportionately, and the corresponding cost reduced, when comparison is made to a full scale system.

The sludge obtained after limestone treatment had to settle for 2 hours before the overflow could be extracted, while 1 hour was sufficient in the case of fly ash, indicating a quicker processing time. Since the fly ash sludge settled fairly rapidly, it was predicted that flocculants will not be necessary, whereas in the case of limestone these are routinely used. Limestone utilisation produced 10 kg of sludge per kg of material used, while with fly ash, the sludge produced amounted to only 2.3 - 2.5 kg per kg of material used. Dewatering of the fly ash sludge was thus more effective. The sludge obtained after limestone treatment only contained ~12 % solids, while the fly ash sludge contained 42 – 45 % solids. Due to improved separation of phases after treatment with fly ash a higher proportion of treated water could be recovered.

Limestone needs to be mined, crushed and purchased at R 97.6 per ton at the time of the investigation (2007). Fly ash alternatively is freely available from the power plants in the vicinity. Limestone needs to be transported for long distances at R 72.4 per ton at the time of the investigation. The transport cost for fly ash was quoted at R 55 per ton by truck at the time (2007) of the investigation. Alternative means of transport, such as by train or by trucks returning after coal delivery, should be considered to reduce costs.

The utilisation of fly ash for AMD treatment will reduce the costs associated with long term storage of fly ash (storage in large dumps, remediation of storage leachate). Fly ash, specifically Kriel fly ash, was most cost effective with regards to neutralisation and sulphate reduction. This cost comparison did not consider the additional costs of the biological process needed after limestone treatment. The costs associated with purchase of material and transport make limestone treatment less cost effective than fly ash, whilst costs using Kriel fly ash were comparative to that of limestone at the various treatment stages. However, the costs for biological sulphate removal are not included and this will raise the costs for limestone treatment.

Potgieter-Vermaak (2006) conducted a comparison of limestone, dolomite and fly ash for the treatment of AMD. The results were similar with regards to the pH achieved in this study and highlighted the fact the fly ash was far more efficient with regards to sulphate removal. The cost comparison conducted, based on only chemical treatment, showed that the running costs for fly ash was almost half that of limestone and dolomite. Cost savings of 48 % could be achieved when fly ash is applied instead of limestone. Akcil and Koldas, (2006) also commented on the inefficiency and complexity of limestone treatment when treating high ferrous iron water.

The results of the comparative study has highlighted the many advantages of utilising fly ash instead of limestone for AMD treatment even though larger volumes of fly ash are required.

6.4 CURRENT LIMESTONE PRACTICE

The treatment of AMD with sulphate concentration of 17 100 mg/l using limestone and fly ash was compared in a simulated study to obtain a circum neutral pH, according to current operational capacity of the liming process at Navigation plant in which AMD with a high sulphate content is treated. The AMD treated is made up of discard dump seepage and rain water stored in the toe dam and referred to as Toeseep water. This water is the same as that experimented with in the large scale experiments

in **Chapter 5**. The integrated treatment plant used at Navigation section of Landau colliery consists of the following treatment stages (Maree *et al.*, 2004):

- CaCO_3 handling and dosing system where CaCO_3 is introduced in the form of slurry.
- CaCO_3 neutralisation (Primary Liming Plant (PLP)), consisting of a fluidised bed reactor and sludge separator. Compressed air is used at this stage for iron oxidation and subsequent precipitation.
- Heating unit where feed water is sprayed through spiral jet nozzles while hot air is flowing upwards.
- Biological sulphate removal using ethanol as the carbon and energy source, H_2S stripping using CO_2 produced during calcium carbonate treatment, aerobic treatment for removal of residual organic material and CaCO_3 precipitation.

The current AMD treatment, typically using limestone as a neutralising agent, has several drawbacks.

- In the primary liming plant (PLP), only neutralisation of AMD takes place. Moderate sulphate removal is achieved, without reduction of toxic elements content. After treatment with limestone, the water generally has a sulphate concentration >3000 mg/l and is not suitable for industrial activities unless it is further treated with the biological process, introducing additional costs. Only after the treatment by the biological plant, which further reduces the saturation index of gypsum, is the quality of water suitable for industrial applications.
- Limestone cannot be stored in a silo due to its high moisture content. It needs to be dosed in slurry form. It is abrasive and contains stones which cause blockages in pipes.
- The recovered water is separated from solids using flocculants, with considerable cost implications.
- The sludge that settles down after treatment is pumped to a lined hazardous waste storage area. Storage costs per annum are estimated to be high. The sludge has a very high water content reducing water recovery.

- The neutralised water needs to be further treated for instance by use of biological systems, where sulphate concentration may be reduced to 250 mg/l. A pre-treatment is required, using a costly agent: lime. The biological process is energy and carbon feed (ethanol) consuming (Greben *et al.*, 2004). It is very sensitive to temperature and pH fluctuations and may take several months to equilibrate after start-up. As the process may result in toxic H₂S release, the redox reactions must be carefully controlled. Moreover, the bacteria used in the process may be pathogenic.

6.5 ADVANTAGES OF SUBSTITUTING LIMESTONE WITH FLY ASH FOR AMD NEUTRALISATION

The advantages of using fly ash instead of limestone for the treatment of AMD would include its lower cost, and the fact that it is readily available in large quantities in close proximity to the coal mine where the acidic waters are found.

In general, the limestone utilised in the neutralisation of AMD needs to be mined and crushed as well as transported for long distances, resulting in wear on infrastructure such as roads, as well as pollution and environmental degradation of mined out source areas, whereas the ash does not require further mining or crushing and is available in close proximity. The utilisation of fly ash for AMD treatment will reduce the cost of environmental rehabilitation associated with the storage of fly ash. The cost of long term ash storage will be reduced or avoided and environmental remediation costs resulting from fly ash leaching while in lagoon storage will also be minimised.

The quality of the recovered water after neutralisation with fly ash was significantly improved, as shown in **Chapter 5**, and thus there may be significant processing advantage in replacement of limestone with fly ash. The percentage sulphate reduction achieved was excellent at bench scale and comparable to membrane systems and ion exchange and better than other chemical treatment regimes discussed in **Chapter 5**. Further stages in the limestone treatment process e.g. flocculation could be eliminated and their cost reduced since the burden of pollutants in the recovered water would be lower. Since the solid residues settle out of suspension very readily, the flocculation stage could be eliminated with potential cost savings.

Depending on the process conditions chosen in the neutralisation process, different qualities of water may be recovered after treatment with fly ash. Should the pH of AMD be brought to approximately pH 6 with fly ash, further treatment of water may be necessary in the sulphate removal process (SRP) to remove the remaining sulphate. It would be more appropriate to raise the pH to between 9 and 10 to remove the major, minor and trace elements to the maximum and thereafter adjust the pH to more circum neutral values for reuse or discharge. Decreasing the pH of the water to required levels will be easily accomplished since the buffering capacity of elements such as iron, aluminium and other toxic metals is reduced as a result of their precipitation as metal hydroxides and subsequent removal in the solid fraction. The quality of the remediated water should make it suitable for reuse and possible release and would minimise its impact on RO and EDR water treatment systems.

The possible reuse, of solid residues resulting from the neutralisation process, as backfill material could provide an answer to the problem of AMD generation. The possibility exists for the production of a durable, stable and environmentally benign fill material in backfilling of mines, by use of the residues already available in bulk on site after the neutralisation process requiring no further purchasing and importation of other suitable material. Long term costly and hazardous waste storage of AMD sludge remaining after limestone treatment would also be avoided. In the long term, it can be expected that the amount of AMD to be treated at the mine will be significantly minimised by preventing air ingress by backfilling the voids left underground after coal extraction. Backfilling will also add to the economic lifetime of mines and allow a greater degree of extraction of coal.

The waste solid residues can furthermore be transformed into zeolite adsorbent. By selling such value added zeolite materials manufactured from the solid residues would represent a source of income. These adsorbents are also excellent at removing toxic elements from water representing another cost saving opportunity by reducing the cost of maintenance and replacement of RO or RO-EDR systems, by reducing the load of dissolved species in waters currently submitted to these systems for polishing.

CHAPTER 7

TREATMENT OF CIRCUM-NEUTRAL MINE WATER

7.1 INTRODUCTION

Circum-neutral mine waters, often referred to as Ca-Mg waters, are produced when acidic mine water undergoes partial neutralisation due to the surrounding geology. If the acidic mine water flows past dolomite rock, it is partially neutralised and in the process some metal contaminants are precipitated while sulphates may precipitate as gypsum or be adsorbed on metal hydroxides. As a result, circum-neutral mine waters contain lower sulphate concentrations than acid mine water and at pH 6.5, the concentration of toxic metals are near or below the acceptable effluent limits. The water does however; contain considerable concentrations of sulphate, calcium, magnesium and manganese (Banks *et al.*, 1997). Coal mining operations in South Africa are known to produce large quantities of circum-neutral water contaminated with a considerable amount of sulphate. As such, in addition to treating acidic mine water, this section describes the treatment of circum-neutral water emanating from the Middleburg mine with fly ash, to ascertain its capacity for sulphate attenuation in Ca-Mg sulphate waters that are naturally low in iron and aluminium..

Circum-neutral mine water from Middleburg mine was collected in 10 l containers and stored under refrigeration to preserve the sample. The mine water was initially analysed to determine its chemical composition (Table 7.1).

Table 7.1: Chemical composition of circum-neutral mine water from Middleburg mine

COMPONENT	CIRCUM-NEUTRAL MINE WATER
pH	7.16
Conductivity (mS/cm)	5.3
Aluminium (mg/l) Al	0.01
Barium (mg/l) Ba	<0.005
Boron (mg/l) B	0.09
Beryllium (mg/l) Be	<0.005
Cadmium (mg/l) Cd	<0.005
Cobalt (mg/l) Co	0.31
Chromium (mg/l) Cr	0.01
Copper (mg/l) Cu	0.02
Iron (mg/l) Fe	0.17
Lead (mg/l) Pb	0.04
Manganese (mg/l) Mn	28
Nickel (mg/l) Ni	0.20
Zinc (mg/l) Zn	0.11
Calcium (mg/l) Ca	480
Magnesium (mg/l) Mg	820
Sodium (mg/l) Na	25
Potassium (mg/l) K	32
Chloride(mg/l) Cl	<0.1
Nitrate (mg/l) NO ₃	<0.1
Sulphate (mg/l) SO ₄	4560

The contamination level of the circum-neutral mine water was not as high as the Toeseep AMD utilised in this study (**Chapter 4**). The pH of the circum-neutral mine was already neutral at 7.16 and the toxic element concentrations were lower than the AMD utilised in this study. The iron and aluminium concentrations of 0.17 and 0.01 mg/l respectively were far lower than the 5000 mg/l and 200 mg/l aluminium

contained in Landau AMD. The anions, calcium, magnesium and in particular sulphate concentrations were elevated.

Experiments were conducted with fly ash from Arnot, Duvha and Hendrina power plants. The experiments were conducted at beaker scale with 500 ml AMD. Fly ash was added to the circum-neutral water with constant stirring. The pH was monitored and the reaction terminated when the pH of the solution reached a pH 9. This was based on findings in **Chapter 5**, where sulphate was reduced significantly at pH >6.0 via adsorption and reduced even further at pH >8.0 due to the formation of Al-Si-Ca-SO₄ rich mineral phases. A further consideration for maintaining a maximum pH of 9 was that for discharge purposes, the pH would again have to be adjusted to neutrality resulting in further costs. As such, the quantity of fly ash applied in the treatment process was based on increasing the pH only slightly to achieve sulphate removal. The ratios applied are tabulated in Table 7.2.

Table 7.2: Selected ratios for treatment of circum-neutral mine water with Arnot and Duvha and Hendrina fly ash

	Ratios of fly ash to mine water		
Arnot fly ash	1:250	1:500	1:1000
Duvha FA	1:250	1:500	1:1000
Hendrina	1:50	1:100	1:250

Much less fly ash was added since the pH of the mine water was neutral. The ratios for Hendrina fly ash were lower than that utilised for Arnot and Duvha fly ash. Lower ratios were applied for the Hendrina fly ash due to its lower CaO content as determined in Chapter 4.

7.2 RESULTS OF FLY ASH TREATMENT OF CIRCUM-NEUTRAL WATER

Figures 7.1-7.4 illustrates the effect of fly ash on the attenuation of sulphate and iron concentration in circum-neutral mine water. The circum-neutral mine waters' initial pH of 7.1 was raised to pH 9.0 within 1 hour at all ratios.

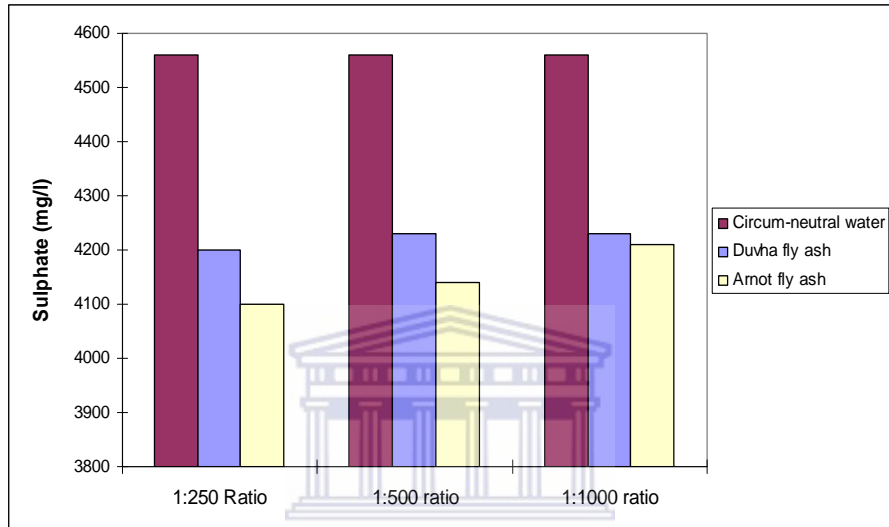


Figure 7.1: Effect of Arnot and Duvha fly ash treatment on sulphate concentration in circum-neutral mine water

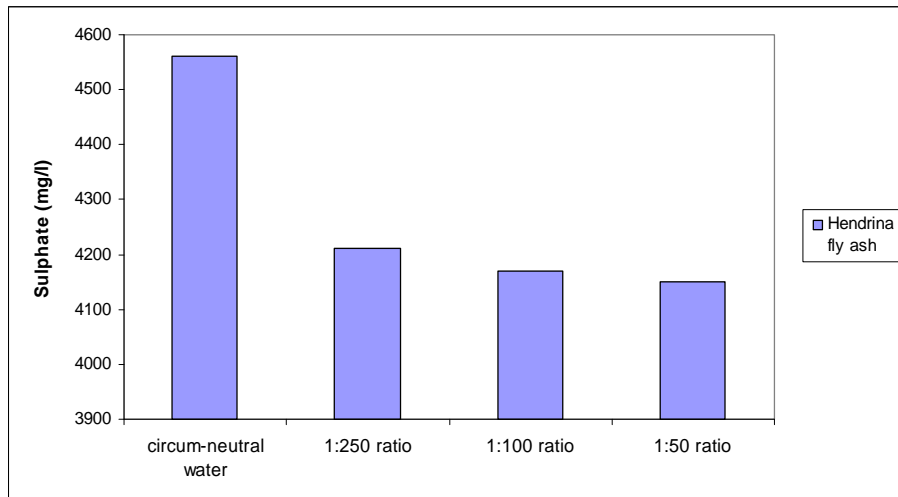


Figure 7.2: Effect of Hendrina fly ash treatment on sulphate concentration in circum-neutral mine water

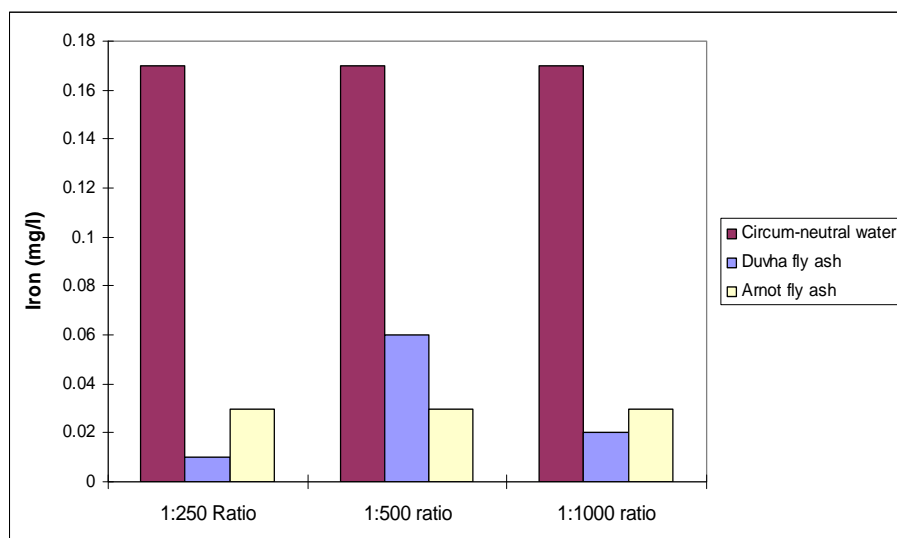


Figure 7.3: Effect of fly ash treatment on iron concentration in circum-neutral mine water at pH 9

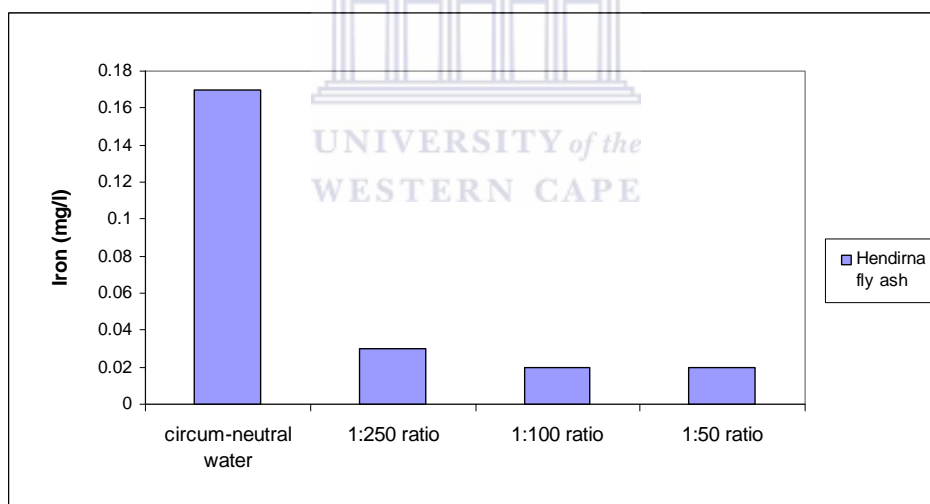


Figure 7.4: Effect of Hendrina fly ash treatment on iron concentration in circum-neutral mine water at pH 9

In previous beaker scale experiments (Chapter 5), a pH > 8.0 resulted in >90 % sulphate reduction, at specific fly ash:AMD ratios. Treatment of circum-neutral mine waters with fly ash did not achieve significant sulphate reductions. Greater quantities of fly ash (lower fly ash:AMD ratios) resulted in more sulphate reduction, but again this was not significant. Duvha and Arnot fly ash achieved a maximum sulphate

reduction of 7.8 % and 10 % respectively at the 1:250 ratio (Figure 7.1). Hendrina fly ash achieved a similar reduction in sulphate of 9 %, but with the smaller ratio of 1:50 (Figure 7.2). This proved that the lower CaO content of Hendrina fly ash renders it less effective, since more fly ash is required than Arnot and Duvha to achieve similar results with regards to sulphate attenuation. The initial iron concentration of 0.17 mg/l in the mine water was almost totally removed by all fly ashes (Figure 7.3, 7.4). Hendrina fly ash was as efficient as Arnot and Duvha fly ash in reducing the iron concentration at the smaller ratios. This low initial iron concentration in the circum-neutral mine water could be an important contributor to the low percentage of sulphate reduction, since at pH values >6.0, high concentrations of sulphate are adsorbed during Fe(OH)₃ precipitation (Gitari *et al.*, 2008). Further, the low amount of fly ash used in the experiments and a pH of 9 could be insufficient to allow sufficient attenuation of sulphate. This phenomenon is explained further by Madzivire *et al.*, (2009) during treatment of circum-neutral mine water. The acidity generated by the formation of aluminium and iron (oxy) hydroxides and oxyhydroxysulphate complexes facilitates lime dissolution and subsequent Ca²⁺ and OH⁻ release. Sulphate attenuation is enhanced via the formation of gypsum when the Ca²⁺ combines with SO₄²⁻ (Madzivire *et al.*, 2009). Further, Madzivire *et al.*, (2009) reported that at pH values >12, sulphate attenuation was enhanced. With larger quantities of fly ash applied, greater concentrations of Ca²⁺ would be available for gypsum precipitation.

7.3 SUMMARY FLY ASH TREATMENT OF CIRCUM-NEUTRAL WATER

Results from the treatment of circum-neutral mine water have shown that, the quality of this type of mine water could also be improved with fly ash. However, sulphate attenuation was not significant in comparison to AMD waters due to two primary factors. The first being the influence of iron and aluminium concentrations, which tend to aid sulphate attenuation via adsorption during precipitation of the (oxy) hydroxides and oxyhydroxysulphate complexes. Secondly, addition of larger quantities of fly ash as were applied in AMD treatment would render more Ca²⁺ available for gypsum precipitation and subsequent sulphate attenuation. The experiments conducted in this study utilised minimum quantities of fly ash, aimed only at increasing the pH to 9.0. As was reported in circum-neutral water treatment

conducted by Madzivire *et al.*, (2009), at pH values >12 , sulphate attenuation was enhanced. Additional experimentation with large quantities of fly ash and higher pH values is recommended as it is expected that more fly ash would increase the pH further and subsequently aid in further sulphate attenuation.



CHAPTER 8

DISCUSSION, CONCLUSIONS AND RECOMMENDATIONS

8.1 INTRODUCTION

This chapter provides a summary of the discussion of results and conclusions drawn. Recommendations and areas for further and future research are made based on the results of this study. The investigations undertaken in this study were initiated due to concerns with regards to the environmental impact of fly ash and the detrimental nature of AMD generated at mines, in particular coal mines. Two major concerns were the highly acidic nature and significant sulphate concentrations of AMD.

The literature study revealed that existing treatment technologies have limited capabilities with respect to sulphate reduction and those that have enhanced capability are associated with exorbitant treatment costs. Mutual beneficiation associated with the application of fly ash for AMD treatment and prevention has demonstrated potential for large scale active neutralisation of AMD. The objectives of this thesis were to determine the effectiveness of utilising fly ash for active AMD neutralisation, sulphate attenuation and the feasibility thereof in comparison to alternate treatment technologies. A further objective was to determine the effect of fly ash treatment on sulphate in circum-neutral waters.

The Mpumalanga coal mining region was selected as the study area due to the abundance of mining that occurs in the region and the localised power plants. The sample streams were selected based on the results of the characterisation study conducted. Beaker scale neutralisation experiments were conducted as a baseline prior to large scale neutralisation experiments. The results at each stage were compared to data obtained from literature. Following the neutralisation experiments, a feasibility study was conducted, comparing fly ash with limestone for AMD neutralisation and treatment. Standard laboratory procedures were applied for the analysis of liquid and solids samples.

8.2 BEAKER AND LARGE SCALE NEUTRALISATION EXPERIMENTS

Beaker scale neutralisation experiments confirmed that fly ash could successfully be applied for the removal of iron and aluminium rich sulphate containing AMD. The relative quantities of soluble bases (oxides) in fly ash and hydrolysable constituents in AMD dictate whether the final solution at a given contact time will have a dominant acid or basic character. The trend that was observed was that the higher volume of fly ash added to AMD, the quicker was the reaction time and the greater the attenuation of sulphate, iron and aluminium. The pH increased with a corresponding decrease in the electrical conductivity, and varied depending on the ratio of fly ash:AMD selected or volume of ash applied: 1:1 (pH 12.9), 1:2 (pH 12.2), 1:3 (pH 11.7), 1:5 (pH 11.1) and 1:10 (pH 9.3). Sulphate was attenuated in excess of 90%, from 5700 mg/l to 120 mg/l, via adsorption during $\text{Fe}(\text{OH})_3$ precipitation and the gypsum formation. Fly ash performance with regards to sulphate attenuation was better than limestone and comparable to membrane and ion exchange treatment technologies. Iron was almost completely removed (>99 %) at pH values >7 via $\text{Fe}(\text{OH})_3$ precipitation. Aluminium also achieved a 99% reduction via the formation of various minerals, primarily gibbsite. Optimum ratios of fly ash:AMD ranged between 1:3 and 1:10.

Large scale neutralisation experiments demonstrated the possibility of applying the fly ash technology at full scale AMD treatment plants. Experimental ratios ranged from 1:3 to 1:10 fly ash:AMD. Comparative experiments showed that the rate of agitation influenced the rate of reaction. With most ratios applied, the final pH was less than that achieved with beaker experiments resulting in lesser sulphate attenuation. The pH ranged from pH 9.9 (1:3 ratio) and pH 7.7 (1:5 ratio). The maximum pH obtained at large scale with the 1:10 ratio was 4.2. It was postulated that changes in fly ash composition and/or mineralogy as well as process conditions, could have influenced the pH values and ultimately the neutralisation process and elemental attenuation. Therefore fly ash treatment process should be adapted for the different qualities of fly ash applied for AMD neutralisation and amelioration. Based on the results of the initial large scale experiments, a 1:6 ratio was selected for further large scale experiments. At this ratio, elemental attenuation trends, similar to those observed in the beaker experiments, were also seen. However, the lower pH values resulted in a

lesser sulphate reduction of only 68 %, even after the long contact time, with a 1:6 ratio and final pH of 6.33. In comparison, the integrated limestone/lime process only achieved a 59 % reduction in sulphate concentration at pH values >12. Greater sulphate reduction is expected with fly ash at the higher pH values as was seen with beaker studies. Reduction of iron and aluminium at this ratio was excellent (>99 %). The LOI, which measures the amount of unburned carbon remaining in the fly ash, was found to influence the neutralisation. Fly ash with high unburned carbon of 6.6 % hindered an increase in pH possible due to reduced free lime content in the fly ash. The presence of high percentages of unburned carbon could be attributable to variations in coal quality, boiler conditions or both. In comparison to the commonly used limestone process, fly ash was capable of raising the pH of the AMD to higher levels thereby reducing sulphate more efficiently.

8.3 FEASIBILITY STUDY OF FLY ASH VERSUS LIMESTONE TREATMENT OF AMD

A comparative study of fly ash versus limestone treatment of AMD was conducted based on the neutralisation potential, sulphate removal and to a smaller degree, costs. Three different fly ash samples namely, Arnot, Hendrina and Kriel fly ash was compared to limestone. In the case of fly ash, a larger mass was used because of the lower CaCO₃ content (13-18 % CaCO₃ for fly ash versus 98 % for limestone) of fly ash for treatment of the very contaminated AMD tested (>17000 mg/l sulphate). Reaction times were comparable for all neutralising material and Kriel fly ash achieved the lowest reaction time. Kriel fly ash achieved 66 % attenuation in sulphate whilst limestone only achieved 43 % at similar pH levels. The reduction in acidity was most pronounced with Kriel fly ash reducing the acidity from 12300 mg/l as CaCO₃ to 1850 mg/l as CaCO₃. When using limestone, the acidity was only reduced to 5120 mg/l as CaCO₃. When the reaction time for the Kriel fly ash was extended, the acidity was almost completely reduced. Settling rates were better with the fly ash which would eliminate the use of flocculants as is currently done with limestone treatment. A higher percentage of water recovery was also achieved with fly ash. Fly ash, more specifically Kriel fly ash, was most cost effective with regards to neutralisation and sulphate. This cost comparison did not consider the additional costs of the biological process that is needed after limestone treatment. The

comparison highlighted the advantages of utilising fly ash in comparison to limestone and demonstrated its cost effectiveness.

8.4 TREATMENT OF CIRCUM-NEUTRAL MINE WATER WITH FLY ASH

In addition to AMD, an abundance of Ca-Mg sulphate rich circum-neutral mine water is also generated during mining operations. Fly ash treatment, aimed at sulphate attenuation was investigated at beaker scale at pre-determined fly ash:AMD ratios. These ratios were much larger using much less fly ash than initial experiments conducted with AMD since the mine water was already neutral and only a slight increase to pH 9 was required. Iron and aluminium were detected in only very low concentrations in the circum-neutral mine water and were almost completely removed after the addition of fly ash. Sulphate attenuation was minimal, decreasing from 4560 mg/l to 4100 mg/l at a 1:250 ratio and a maximum 10 % in attenuation was achieved. The explanation behind this was 1) the restricted amount of fly ash added and low pH did not allow sufficient gypsum precipitation and 2) the low iron concentration inhibited sulphate adsorption which occurs during $\text{Fe}(\text{OH})_3$ precipitation. With larger volumes of fly ash applied, greater concentrations of Ca^{2+} would be available for gypsum precipitation.

8.5 RECOMMENDATIONS

In order to further elucidate aspects of the fly ash treatment technology, the following recommendations are put forward:

- More experimental work needs to be conducted at large scale, with larger fly ash volumes to attain higher pH values to ascertain optimum sulphate attenuation capabilities. Automatic data logging is recommended to identify optimum contact times and associated changes in pH.
- Further neutralisation experiments need to be conducted to determine the maximum percentage unburned carbon in fly ash that will be tolerable for neutralisation.

- Additional neutralisation experiments, using a wider range of fly ash from various sources would aid in delimiting the optimum conditions necessary for neutralisation.
- Additional neutralisation experiments with Ca-Mg sulphate rich circum-neutral mine water, with the addition of larger volumes of fly ash to achieve pH values >9.0. This will elucidate the sulphate attenuation capabilities of fly ash in circum-neutral mine waters.
- Test the fly ash treatment technology at pilot scale.

8.6 SIGNIFICANCE OF THE STUDY

The results of this study have shown that fly ash could be successfully applied for the neutralisation of acid mine drainage (AMD) and effectively reduce the sulphate load in the treated water. Iron and aluminium which was also present in significant concentrations was almost completely removed. In comparison to alternate treatment technologies, fly ash performance with respect to sulphate attenuation, was more effective than the conventionally applied limestone treatment and was comparable to technologies like membrane system and ion exchange. Fly ash thus provides for a cost efficient, alternate technology for AMD neutralisation and amelioration. Treatment of fly ash with AMD has the simultaneous advantage of neutralising two sources of waste streams.

The large scale experiments have shown the potential to apply this technology at pilot and full scale plants. Further, this technology has shown the potential to treat circum-neutral mine waters.

The limitation of the technology lies with the quality of fly ash and AMD. Variations in the chemical composition and mineralogy of fly ash could influence the neutralisation reaction and the same is true if the AMD quality varies. Thus,

operating conditions may have to be adapted and process controls at full scale treatments are necessary



CHAPTER 9

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**APPENDIX A: DETERMINATION OF ALKALINITY OF WATER
ELECTROMETRIC TITRATION**

METHOD NUMBER 304	PAGE 1 OF 3
REV 6	

**DETERMINATION OF ALKALINITY OF WATER
ELECTROMETRIC TITRATION**

BASIS OF METHOD

This method covers the rapid, routine control measurement of alkalinity to predesignated end points of waters that contain no materials that buffer at the end point or other materials that interfere with titration by reason of colour, precipitation, etc.

The sample is titrated with standard acid to a designated pH, the end point being determined electrometrically.

INTERFERENCES

1. Suspended solids may interfere in electrometric titrations by making the glass electrode sluggish.
2. Similarly, the development of a precipitate during titration may make the glass electrode sluggish and cause high results.
3. Variable results may be experienced with waters containing oxidising or reducing substances, depending on the equilibrium conditions and the manner in which the sample is handled.
4. Although oily matter, soaps, suspended solids and other waste materials may interfere with the pH measurement, these materials may not be removed to increase precision, because some are an important component of the acid- or alkali-consuming property of the sample.

SAMPLE PREPARATION

The analysis should be carried out as soon as possible after sampling: No sample preparation is required.

TIME REQUIRED FOR ANALYSIS

Approximately 6 minutes per sample, although this may vary considerably from sample to sample.

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REV 6	

REAGENTS

1. 0.02 N HNO₃: Measure 1.4 ml of 65 % HNO₃ into a 50 ml of milli-q water. Precautionary measures must be taken handling acid. Cool, and make up to the mark in a 1000 ml volumetric flask.
2. Standardise the 0.02 N HNO₃ against 0.02 N sodium carbonate.
3. 0.002 N sodium carbonate for standardisation: Weigh 1.06 g of sodium carbonate and dissolve in UHP water and make up to the mark in a 1000 ml volumetric flask.
4. 0.002 N QC Standard: Weigh 1.06 g of sodium carbonate and dissolve in UHP water and make up to the mark in a 1000 ml volumetric flask.

ANALYTICAL PROCEDURE

1. Calibrate the instrument as instructed in method 300.
2. Pipette 25 ml of sample into a beaker and adjust the temperature to 25°C ± 2°C as per method 300.
3. Analyse the QC standard before analysing the samples and check that the results are within the limits of the control chart.
4. If required, flush the assembly until no more bubbles appear in the titration tube.
5. Press <user method> on keyboard and recall method will appear on the screen. Press 11 and <enter>.
6. On the screen "set pH" will appear on the screen and then press <start>.
7. The instrument will start the titration with 0.02 N HNO₃ automatically, until the end points are reached.
8. Alkalinity results displayed as follows:
RS1 = "P Alkalinity"
RS2 = "M Alkalinity"
RS3 = "Total Alkalinity"
9. All samples are analysed in duplicate.
10. If alkalinity is very high, pipette 5 ml of the sample and continue as per step 5. The supervisor must be notified prior to analysis to change instrument settings. The final results are calculated automatically by the instrument.
11. If alkalinity is still too high titrate 5 ml of sample with standardised 0.2 N HNO₃. The supervisor must be notified prior to analysis to change instrument settings. The final results are calculated automatically by the instrument.

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VALIDATION OF ANALYTICAL DATA

Analytical data is validated according to procedure P529.

REFERENCES

Standard Methods for the Examination of water and Wastewater 20th edition 1998, pp 2-26.
Instruction Manual for Metrohm 702 SM Titrimo

COMPILED BY: _____ DATE: _____
D Surrender (QC Co-ordinator)

AUTHORISED BY: _____ DATE: _____
J Reeves (QA Manager)



APPENDIX B: DETERMINATION OF ANIONS IN WATER BY ION CHROMATOGRAPHY WITH CONDUCTIVITY MEASUREMENTS: CHROMATOGRAPHIC METHOD

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DETERMINATION OF ANIONS IN WATER BY ION CHROMATOGRAPHY WITH CONDUCTIVITY MEASUREMENTS CHROMATOGRAPHIC METHOD

BASIS OF METHOD

A water sample is injected into a stream of carbonate-bicarbonate eluant and passed through a series of ion exchangers. The anions of interest are separated on the basis of their relative affinities for a low capacity, strongly basic anion exchanger (guard and separator column). The separated anions are directed onto a strongly acidic cation exchanger (suppressor column) where they are converted to their highly conductive acid form and the carbonate-bicarbonate eluant is converted to weakly conductive carbonic acid. The separated anions in their acid form are measured by conductivity. They are identified on the basis of retention time as compared to standards. Quantity is preformed by measurement of peak area or peak height.

This gives the parameters for the use of a Dionex type AS14 anion separator and AG14 anion guard column set using a microbore (2mm ID) system. This column set offers improved separation of all analytes but with a similar analysis time to the AS4A type column set, and shorter analysis time than the AS12A type column set.

INTERFERENCES

1. Any substance that has a retention time coinciding with that of any anion to be determined will interfere.
2. A high concentration on any one ion interferes with the resolution and retention characteristics of other anions.
3. Spurious peaks may result from contaminants in reagent water, glassware, or sample processing apparatus.
4. Organic species, if present, will interfere with the fluoride ion.

SAMPLE PREPARATION

1. Remove sample particulates by filtering through a pre-washed 0.2 μm pore diameter membrane filter.
2. The sample may require dilution in order for the anion values to be as close as possible to the standard values.

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TIME REQUIRED FOR ANALYSIS

- ± 20 minutes for instrument stabilisation
- ± 15 minutes per calibration run
- ± 15 minutes per sample run

SPECIAL APPARATUS

1. ICS-1500 Ion chromatograph Unit operating on Chromeleon Software, comprises of an injection valve, a sample concentration column, a temperature-compensated small-volume conductivity cell, and a personal computer. The ion chromatograph shall be capable of 0.05 to 2.50 ml.min⁻¹ eluent at a pressure of 1 400 to 6.900 kPa.
2. An inject valve with sample loop (2µl) and a temperature-compensated small-volume conductivity cell.
3. Anion separator column (Dionex type AS14 column is suitable) with styrene divinylbenzene-based low-capacity pellicular anion-exchange resin capable of resolving Cl⁻, F⁻, NO₃⁻, NO₂⁻, Br⁻, and SO₄²⁻, with column length of 2 x 250 mm.
4. Guard column (Dionex type AG14 column is suitable), identical to separator column except 2 x 50 mm, to protect separator column from fouling by particulates or organics.
5. Anion micromembrane suppressor or anion self-regenerating suppressor for removal of cations from the eluent stream.
6. An electronic integrator or computer-based integration station.

REAGENTS

1. Deionised water with a conductivity of less than 0.5 µScm⁻¹ and filtered through a 0.22 µm membrane filter to remove particulates.
2. Eluent solution: (See manufacturers recommendations for the particular column set used.) For the Dionex type AS14 and AG14 set use 1.0 mM sodium bicarbonate and 3.5 mM sodium carbonate. Weigh 8.4 g sodium bicarbonate and 37.1 g sodium carbonate into a beaker and dissolve in deionised water. Dilute the solution to 500 ml with deionised water. This stock may be kept for 1 year in a polypropylene bottle. Pipette 20 ml of this stock into a 2 litre volumetric flask, dilute to volume with deionised water, mix well and transfer to the eluent reservoir.

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3. Reagent solution 0.025 N, H₂SO₄. Measure 27 ml of concentrated H₂SO₄ (measuring cylinder) and slowly (observing safety requirements for acids) add to a beaker containing approximately 300 ml deionised water. Dilute to 1 l (this is approximately 1 N). dilute 100 ml of this solution to 4 l with deionised water (NB this reagent is not required if electronic suppression is available).
4. Standard anion solutions, 1 000 mg l⁻¹. Prepare a series of standard anion solutions by weighing the indicated amount of salt, dried to a constant weight at 105 °C and dissolved in 1 000 ml of demineralised water. The salts used for the preparation of the standards must be of the best quality ie GUARANTEED REAGENT (GR Grade) from Merck, ANALYTICAL REAGENT (AR Grade) from Riedel-de Haen or a suitable supplier. Store in plastic bottles in a refrigerator, these solutions are stable for at least 1 year.

Anion	Salt	Amount (g.l ⁻¹)
Cl ⁻	NaCl	1.6485
NO ₃ ⁻	NaNO ₃	1.3707
NO ₂ ⁻	NaNO ₂	1.4998
SO ₄ ²⁻	Na ₂ SO ₄	1.4785

5. Combined working standard solution 1: Pipette the following volumes of the standard solutions (prepared in 4) into a 1 l volumetric flask.

Cl ⁻	50.0 ml	(50.0 mg l ⁻¹)
NO ₂ ⁻	10.0 ml	(10.0 mg l ⁻¹)
NO ₃ ⁻	25.0 ml	(25.0 mg l ⁻¹)
SO ₄ ²⁻	100.0 ml	(100 mg l ⁻¹)

6. Remaining work standards. Pipette 50.0 ml aliquots of Standard Solution 1 into each of the volumetric flasks given below, and dilute to volume the concentrations of the solutions are in brackets.

Standard Volumetric Flask	2 100.0 ml	3 250 ml	4 500 ml	5 1 000 ml
Cl ⁻	25.0	10.0	5.0	2.5
NO ₂ ⁻	5.0	2.0	1.0	0.5
NO ₃ ⁻	12.5	5.0	2.5	1.25
SO ₄ ²⁻	50.0	20.0	10.0	5.0

The working standards must be prepared weekly.

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ANALYTICAL PROCEDURE

1. Prepare System

Set up the ion chromatograph according to the operation manual, using the following conditions:

Flow rate : 1.20 ml.min⁻¹
 Suppressor : 31mA
 Cell Heater : 35°C

Set up the integrator or data station according to the appropriate operation manual. (For integrators, a chart speed of 0.5 cm.min⁻¹ and attenuation of 256, 512, or 1024 mV is usually suitable.) Adjust other parameters after the first injection, using the procedure recommended in the operation manual. Allow to equilibrate to a stable pressure and conductivity reading. With the conditions given the pressure should be between 200-3000 psi and conductivity 17-20 µS.cm⁻¹. Offset the conductivity to zero.

2. Calibrate System

Using a disposable syringe, or by autosampler if available, inject a portion of standard 3 into the ion chromatograph. When the chromatogram is complete, use the peak retention data to set up the calibration parameters in the integrator or data station (refer to the operation manual). The calibration is stable for one week.

For the Dionex AS14 column type, the approximate retention times are:

Cl ⁻	4.55 minutes
NO ₂ ⁻	5.61 minutes
NO ₃ ⁻	8.99 minutes
SO ₄ ²⁻	12.60 minutes

Perform a 5-point calibration by injecting each of the standards in turn as required by the calibration programme.

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3. Analysing of Samples

Steps to be followed:

- 3.1 Sort samples according to logging-in sequence and pour into the sample vials in the sample tray.
- 3.2 Switch on the computer, printer, autosampler and the ion chromatography system.
- 3.3 Check the chromeleon server on the right side of the computer, it will take about 1 minute to start.
- 3.4 When the chromeleon server is running idle, double click on the chromeleon icon. NB. A problem may arise with starting of the server but that may be rectified by putting the Dongel (green piece of metal) in and out at the back of the CPU.
- 3.5 Click on panels
- 3.6 Click on ICS-1500 system AS40 panel.
- 3.7 Click on start up, the message (Pump ECD Devise is not remote) will appear, and then press OK.
- 3.8 Click on connected, then start up again.
- 3.9 The pump will switch on and the system will take about 20 minutes to stabilize.
- 3.10 Simultaneously press CONTROL and TAB buttons.
- 3.11 Click on sequence, then select the month of the sequence on which samples should be run. Once the sequence has been sorted out, the analysis can be started by clicking on BATCH START and then START THE SAMPLE BATCH.
- 3.12 After the run has been completed, check if any of the analysed peaks exceed the highest calibration concentration for that then make appropriate dilutions and then analyze again.

4. Reporting of Results

Value obtained	Report to
Below LOD	If result is less than the LOD report as less than the LOD of this method
Between LOD and < 100 mg/l	1 decimal places
Between 100 mg/l and < 1000 mg/l	To the nearest ten
Above 1000 mg/l	To the nearest hundred

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CALCULATIONS

No calculations are required, as the concentrations are calculated directly by the personal computer. However, remember to account for any dilutions that may have been made.

SAMPLE STORAGE AND PRESERVATION

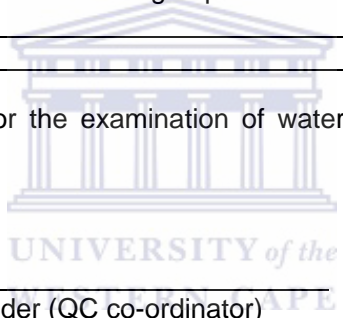
On-line analysis should be performed as close to the sample point as possible keeping the sample line as short as possible. See Procedure P511.

VALIDATION OF ANALYTICAL DATA

Analytical data validated according to procedure P529.

REFERENCES

Standard Methods for the examination of water and wastewater 20th Edition, page 4-6



COMPILED BY: _____ DATE: _____
D Surender (QC co-ordinator)

AUTHORISED BY: _____ DATE: _____
J Reeves (QA Manager)

APPENDIX C: METAL ANALYSIS OF RAW, POTABLE AND WASTE WATER BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY (ICP)

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METAL ANALYSIS OF RAW, POTABLE AND WASTE WATER BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY (ICP)

BASIS OF METHOD

Measurement of atomic emission by optical spectroscopy. Nebulization of samples and transportation of the aerosol produced to the plasma torch, where excitation occurs. Production of characteristic atomic-line emission spectra by a radio frequency inductively coupled plasma (ICP) and monitoring of the intensity of the lines by means of a charge injection device. Processing and controlling of the photon current from the charge injection device by the computer system. Use of the background correction technique to compensate for variable background contribution to the determination of the elements. This method is for the determination metal elements in raw, potable and wastewater using OPTIMA 5300DV instrument.

SAFETY PRECAUTIONS

The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound needs to be treated as a potential health hazard. From this viewpoint, reduce exposure to these chemicals to the lowest possible level by whatever means available.

Wear gloves and safety spectacles when handling concentrated acids.

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RANGE OF APPLICATION

Table 1: List elements, for which this method applies, along with the wavelength, range and detection limit.

Element	λ (nm)	Range (mg/l)	LOD (ppm)
Al	396.1	0-1	0.005
B	208.8	0-10	0.004
Ba	233.5	0-10	0.005
Be	234.8	0-1	0.005
Cd	226.5	0-10	0.005
Co	228.6	0-10	0.005
Cr	267.7	0-10	0.005
Cu	324.7	0-10	0.005
Fe	259.9	0-10	0.005
Mn	260.5	0-10	0.005
Ni	231.6	0-10	0.005
Pb	220.3	0-10	0.007
Sr	407.7	0-0.5	0.005
Zn	213.8	0-10	0.005

For the purpose of this method, total metals are defined as soluble metals at pH<2.

The analytical range of this manual has been restricted to improve performance. Samples that do not fall within the ranges as specified in Table 1, will be diluted with deionized water, until they do.

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INTERFERENCES

The method is free from inter-elemental interferences, as the spectral lines chosen are free from interference.

SAMPLE PREPARATION

1. Glassware, sample vessels, reagents, standards and blank solution

All volumetric glassware (pipettes and volumetric flasks only), should be of grade A quality. Glassware should be cleaned by rinsing with 1:9 (v/v) nitric acid, followed by deionized water before use. All storage containers for standard solutions should be soaked in 1:9 (v/v) nitric acid overnight and rinsed with deionized water before use. All sample vessels to be rinsed with demineralised water. Before use, each sample vessel should be rinsed at least once with at least 5 ml of the solution to be analysed.

Water used for dilutions, should have an element content that is negligible, compared to the smallest concentrations to be determined in the samples. Deionized water is suitable for this purpose.

2. Nitric acid

To prevent the possible introduction of foreign mineral contaminants, acid of at least analytical reagent grade is required.

REAGENTS

1. Metal stock solution

Ampoules /ready-made standard solutions containing the different elements are commercially available and are made up according to the recommendations of the manufacturer. All materials bought are, where possible, traceable to reference materials. Shelf life is two years, if stored in high quality polyethylene containers.

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2. Multi-element standard solution (prepared by analyst)

HIGH STD: Prepared by pipetting 10ml of 1000mg/L stock of each element into a 1000ml volumetric flask. For Al and Be a 100ml of a 10mg/L prepared standard is pipetted. For Sr a 50ml of a prepared 10mg/L standard is pipetted. 4ml HNO₃ is added to the 1000ml volumetric flask and made up in deionized water. Store in DURAN PYREX glass bottles. Shelf life is 12 months.

NEW STD: Prepared by pipetting 200ml of the HIGH STD into a 1000ml volumetric flask, 4ml HNO₃ is added and made up in deionized water. Store in DURAN PYREX glass bottles. Shelf life is 12 months.

<i>Element</i>	HIGH STD(mg/l)	NEW STD(mg/l)
Al	1.0	0.2
B	10.0	2.0
Ba	10.0	2.0
Be	1.0	0.2
Cd	10.0	2.0
Co	10.0	2.0
Cr	10.0	2.0
Cu	10.0	2.0
Fe	10.0	2.0
Mn	10.0	2.0
Ni	10.0	2.0
Pb	10.0	2.0
Sr	0.5	0.1
Zn	10.0	2.0

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3. Multi-element quality check standard solution (prepared by analyst)

HIGH STD (FOR THE QC): Prepared by pipetting 10ml of a 1000mg/l of each element into a 1000ml volumetric flask, except Al and Be of which 1ml of each is pipetted, 4ml HNO₃ is added and made up in deionized water. Store in DURAN PYREX glass bottles. Shelf life is 12 months.

QC: Prepared by pipetting 100ml of the HIGH QC STD into a 1000ml volumetric flask, 4ml HNO₃ is added and made up in deionized water. Store in DURAN PYREX glass bottles. Shelf life is 12 months.

<i>Element</i>	(QC) mg/l
Al	0.1
B	1.0
Ba	1.0
Be	0.1
Cd	1.0
Co	1.0
Cr	1.0
Cu	1.0
Fe	1.0
Mn	1.0
Ni	1.0
Pb	1.0
Sr	0.2
Zn	1.0

4. Blank solution (4 ml HNO₃/l prepared by Analyst)

2 ml of nitric acid made up to 500 ml. Store in a DURAN PYREX glass bottle.

5. Argon gas

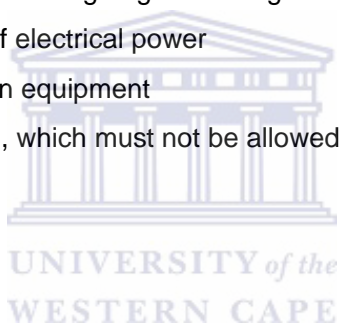
Spectrographic grade argon gas at a regulated pressure of above 700 kPa (Minitank)

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ANALYTICAL PROCEDURE

1. Equipment

- The OPTIMA 5300DV SPECTROPHOTOMETER, which includes the ICP Emission Source and the Optical system
- The host computer and printer
- AS 93PLUS Autosampler
- The recirculator and refrigeration unit(chiller) for the SCD Detector
- Atlas Copco Compressor
- Spectrographic grade argon gas at a regulated pressure of 700 kPa.
- Suitable source of electrical power
- Suitable extraction equipment
- Suitable drainage, which must not be allowed to overflow



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2. Procedure

- 2.1 The steps described in 2.3 should, if followed in sequence, generally lead to satisfactory accomplishment of the task, but may not always be the most efficient approach. Analysts should take note that certain parts of the sequence should normally be carried out in the specified order. Groups can usually be swapped around to obtain better efficiency. The torch compartment will purge with argon for about 45 seconds, before attempting to ignite the plasma (this time delay is computer controlled).
- 2.2 Experience has demonstrated that failure of this method to perform satisfactorily can rarely be ascribed to human error. It is usually caused by instrumental malfunction. The nature of such malfunctioning is often unique, and beyond the scope of this method, or even that of the THERMO JARRELL ASH User's Guide. When problems are encountered, they should be discussed with other authorised users, or the service engineer, as indicated in the Instrument Logbook. An entry to this effect should also be made in the instrument Logbook.

3. Steps

1. Sort samples according to registration sequence.
2. Confirm that there is power to the refrigeration unit.
3. Confirm that there is sufficient Argon gas pressure in the lines by noting the reading on the pressure gauge. It must be 550 kPa or more
4. If it is not, then the Argon mini tanks must be checked.
5. Confirm that there is extraction by observing the draught meter above the spectrometer in the clean lab. It must read around 300 Pascals.
6. Should there have been a general power failure, note that the switch on sequence is as follows:
 - GAS
 - CHILLER
 - COMPRESSOR
 - INSTRUMENT
 - COMPUTER
7. Switch on the computer.
8. On the desktop, double click on **WINLAN 32** to load the software.
9. A **DIGNOSTICS** window will confirm the communication between the **AUTOSAMPLER, RF GENERATOR** and **COMPUTER**. Then it will disappear, if not then an error message will appear, attend to the problem on the error message and the wait for the communication to be established, if this is not successful then proceed to step 54.
10. Using the mouse, click on the **PLASMA CONTROL PANEL** icon.
11. This will bring up an information window confirming the status of the controller and the plasma discharge.

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12. Check that the settings are: **RF POWER** – 1300 Watts, **AUXILIARY FLOW** – 0.2 L/min, **NEBULIZER FLOW** – 0.75 L/min, **PUMP RATE** – 2.5 ml/min.
13. Click **ON**, to ignite plasma.
14. If this is not successful then an error message will appear, click on **OK** and the **PLASMA CONTROL PANEL** will reappear. Then try igniting again, if this is not successful then proceeds to step 54.
15. Autosampler table must be loaded to the **OPTIMA 5300DV** computer
16. To do this, click on the **SAMPLE INFO** icon. This will bring up a sample information editor window.
17. Click on **SAMPLE ID** column, start typing the sample information, i.e. **Submission Id, Sample Id** and **User Id**
18. Continue typing according to the LIMS sequence until all the samples have been entered
19. Now right click on the **AUTOSAMPLER LOCATION** column, select **COLUMN FILL** from the drop down menu window will open where a starting location and the sample number range has to be entered. Click **OK** and the location of the sample will be calculated automatically.
20. From the menu select **FILE SAVE AS**, select **SAMPLE INFO FILE** and name the file **SET1B** and then print the sample list and use the list to pour out samples.
21. From the menu click **FILE** then **OPEN- METHOD**, then a method window will pop up, then select **SET1B** then **OK**.
22. Click on **METHOD EDITOR** icon then a window will open.
23. Confirm that **WASH** is set on **BETWEEN SAMPLES** and that the rinse time is at least 30seconds by clicking on sampler then autosampler. Then close the method editor window.
24. Click on **AUTO** icon and select **SET UP**, confirm that the method name is **SET1B** and the sample info is **SET1B**.
25. Confirm that the data is being saved by checking the **SAVE DATA**, double click on open and name the table as would like data to be saved.
26. If it is an unattended run, double click on **SET** under **AUTOSHUTDOWN**, a window will appear then check the **SHUTDOWN** box and select the option required after an automated analysis.
27. Confirm that the **wash before shutdown** and **turn off plasma and pump** boxes have been checked if it is an overnight run.
28. Now select **ANALYZE** from the **AUTO** window, click on **REBUILD LIST** to load the new sample info table.
29. Confirm the sample and standard / QC positions on the autosampler racks.
30. Place the samples, standards and QC's in the relevant positions on the autosampler racks. Ensure that there is sufficient solution in each vial and that the vials are correctly placed in their positions to avoid unnecessary repeats.
31. Confirm that there is sufficient water in the rinse station reservoir.

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32. Remember that each sample vessel should be rinsed at least once with at least 5 ml of the solution to be analysed
33. Check sample transport system for air bubbles, leaks and smoothness of transport. Rectify any problems before continuing.
34. Then click on **ANALYSE ALL** to start running the samples.
35. If this is to be an unattended overnight run then ensure that the terminating action selected is **SHUTDOWN**.
36. As the run begins, check that all the components are functioning properly.
37. When the run has been completed click on **OK**. For an overnight run the instrument will shut down automatically.
38. Ensure that the plasma has been rinsed with UHP water for at least 2-3 minutes.
39. Switch the plasma power supply (RF power) off, using the **PLASMA CONTROL** icon and clicking on **OFF**. An audible click will be heard, do not worry, this is normal.
40. Unclamp the feeder tubes.
41. Unclamp and turn off the rinse station pump.
42. Sign and update printout results.
43. Take the samples found to be out of range and dilute as required.
44. Re-run these dilutions and do not forget to add the dilution factor in the sample table.
45. **File the raw data and send the report.**
46. The OPTIM 5300DV follows the following autosampler protocol.
47. The first step is to standardise all elements in the method.
48. The next step is to analyse a quality control sample.
49. Should the QC fail then it will re-analyse the quality control, should the QC fail again then it will re-standardise all the elements. It will then analyse the QC again. Should it fail a third time, it will re-analyse for the fourth time, if it fails then it will stop. At this stage try solving the problem and restart the run and should it fail again repeat it once more using a different set of standards. Should this prove unsuccessful proceed to step 54.
50. Should it have passed the QC at any stage, the programme will proceed with analysing the first 20 samples.
51. After which it will then analyse another QC. If this QC passes it will analyse the next 20 samples and continue in this manner until the run is completed. At the completion of the run a QC will be analysed.
52. If at any time a QC should fail, the instrument will re-standardise all the elements and analyse the QC again. If the QC passes it will RE ANALYSE the previous 20 samples. Should the QC still fail, it will read the QC once more. Should the QC now pass it will RE-ANALYSE the previous 20 samples, but should it have failed it will stop the autosampler run.
53. Any failures linked to gross errors such as plasma shutoff, empty QC vials; etc must not be entered into the spreadsheet, as they will cause artificial widening of the limits.
54. Contact the local service engineers at PERKIN ELMER at the telephone number stated in the logbook.

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In order to ease the above procedure (not replace it) a checklist (WAC FORM NO.6, REV.2) has been devised and must be utilised before every calibration. These checklists must be filed.

Final reporting policy

Value obtained	Report to
Below LOD	If result is less than the LOD report as less than the LOD of this method
Between LOD and < 1 mg/l	2 decimal places
Between 1 mg/l and < 10 mg/l	1 decimal place
Between 10 mg/l and < 100 mg/l	To the nearest unit
Between 100 mg/l and < 1000 mg/l	To the nearest ten
Above 1000 mg/l	To the nearest hundred

REFERENCE

- 1.0 OPTIMA 5000 SERIES Hardware Guide.
Preliminary Part Number: 0993-7625
Publication Date: April 2004
- 2.0 Concepts, Instrumentation and Techniques in ICP-OES
By Charles B. Boss and Kenneth J. Fredeen.

VALIDATION OF ANALYTICAL DATA

Refer to procedure P506.

COMPILED BY: _____ DATE: _____

AUTHORISED BY: _____ DATE: _____