MINEMAKERS
LIMITED
ABN 48 116 296 541

RETENTION LICENCE RL10/1988

MOINA, TASMANIA

ANNUAL REPORT TO 21 SEPTEMBER 2007

Andrew Drummond
Perth

CONTENTS

APPENDICES

FIGURES

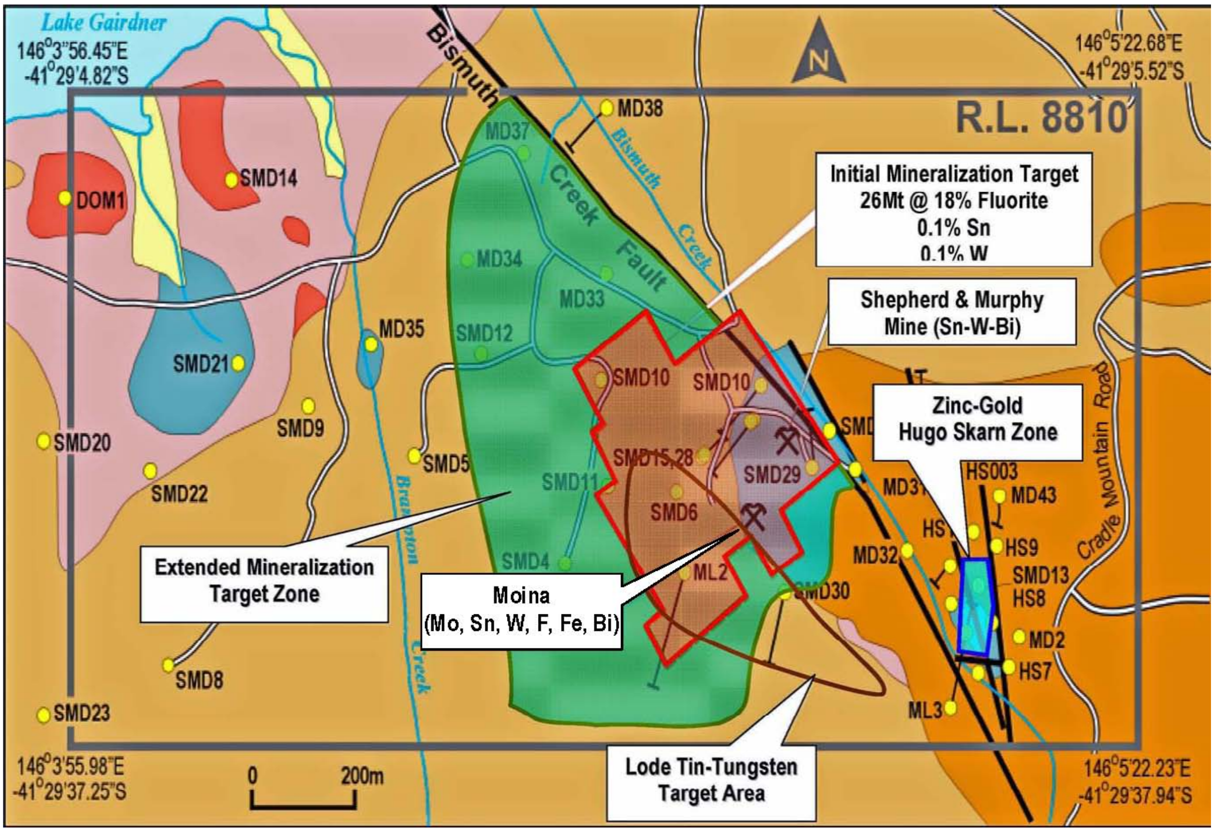
1. BACKGROUND AND TENURE

RL10/1988 was granted on 24 October 1988 to Geotech International Pty Ltd and is renewable annually. As it is a Retention Licence there is no formal minimum expenditure requirement, however an Expenditure Statement is presented in Section 8.

The tenement is managed by Minemakers Ltd, through an option agreement between Geotech and Minemakers' wholly owned subsidiary, Minemakers Australia NL.

Tenement and geological information are presented in Figure 1.

FIGURE 1: MOINA TENEMENT AND GEOLOGY MAP



2. PROJECT VIABILITY OVERVIEW

(a) A 2006 review of all past metallurgical testwork by a metallurgical consultant indicated that extraction of market-acceptable fluorspar from the complex Moina ore would be difficult. Since the early metallurgical investigations by Comalco in the late 1970s to early 1980s there had been no new advances in processing likely to overcome the problems that Comalco identified.

(b) Moina mineralization is complex featuring, as well as fluorite:

- Magnetite
- Tungsten as scheelite
- Tin (but mainly in solid solution in garnet)
- Various sulphides, but particularly those of Zn, Bi and Mo
- Minor gold
- Garnet

(c) In accordance with the general trend to strongly increased metal or mineral commodity prices over the last few years, the Moina mineralization components have seen the following approximate increases:

- Magnetite - quadrupled
- Tungsten - tripled
- Tin - doubled
- Zinc - tripled
- Bismuth - Up 400%
- Molybdenum - Up 500%
- Fluorspar - Up 30%

However, Moina contains no individual component at a sufficiently high level for it to be a stand alone, one commodity producer.

(d) Minemakers has adopted a holistic approach to evaluation of Moina. That is, it aims to assess it as a potential multi-commodity producer. It aims to maximise the net return from mining and processing the deposit, allowing for optimisation of capital requirements and operating costs.

(e) Some introductory comments on recovery of the various components, and their significance, now follow:

- Magnetite can be liberated by the standard grinding process, followed by magnetic separation. The aim is to attain the right grain size to minimise contamination by, and loss of, other components.

- The sulphides should be able to be recovered as a concentrate by flotation.

- Scheelite is potentially recoverable by flotation, as is fluorspar.

- Introductory meetings have been held with Metals X concerning the potential to process garnet in its planned Renison fuming plant. Testwork should be carried out in 2007-2008.

- A gravity circuit should recover some of the tin, tungsten and gold.

(f) In view of the total amount of mineralization, its high fluorspar proportion and the potential for Moina to become a significant fluorspar producer on a world scale, the evaluation of it was initially centred upon that product, with other commodities being viewed as potential co-products.

3. FLUORSPAR OVERVIEW

So as to present the Moina project to the world, so to speak, a paper on it was delivered to the Fluorspar 2006 Conference in Las Vegas, with the aims of:

- Measuring the industry's opinion of the potential of the project.
- Looking for the appropriate way to carry the Project forward.
- Gaining a better understanding of fluorspar's future potential.

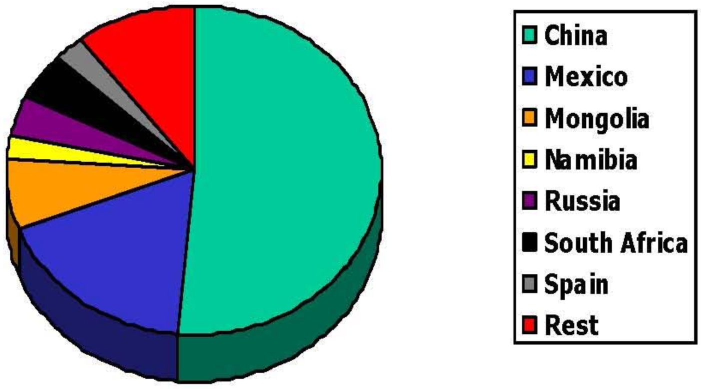
(a) It was evident that fluorspar has a good future as an essential commodity, with a projected growth of 3-4% compound, and a supply problem.

Figure 2 shows world distribution of fluorspar production by country. China dominates, and its recent cutbacks on raw mineral commodity exports have led to Western World uncertainty concerning long-term supply certainty.

(b) Fluorspar price has responded to this and in mid 2007 it has reportedly risen by 30% on 2005 international prices.

FIGURE 2 FLUORSPAR WORLD PRODUCTION 2006

	t
CHINA	2,750
MEXICO	950
MONGOLIA	370
NAMIBIA	127
RUSSIA	210
SOUTH AFRICA	240
SPAIN	150
REST	555
TOTAL	5,350 t



4. DELTA MINERALS PTY LTD

Via the Fluorspar 2006 Conference, contact was made with leading world fluorspar industry expert, Malcolm Crawford, based in Britain and trading as Delta Minerals Pty Ltd. Delta was granted the assignment of reviewing the historic fluorspar investigations so as to undertake a fatal flaw overview. Should the Project not be fatally flawed, then Delta was to recommend an appropriate way to advance it.

The Delta Report is presented as Appendix 1 and the conclusions are reproduced as follows:

- *In the opinion of Delta Minerals, processing of Moina wrigglite will be difficult, but not fatally flawed. It is flawed in the sense that the production of an acidgrade concentrate which meets all international specifications is likely to be impossible, however this does not prevent HF and* AlF_3 *from being produced from a sub-acidgrade Moina fluorspar concentrate in HF plants specifically geared and tuned to accept this grade of fluorspar. As a supplier to compatible HF/*AlF_3 *plants, the Moina project has a strong potential, but as a stand-alone fluorspar producer feeding the international market, the project is fatally flawed, despite many advances in processing technology since the previous testwork in the 1970s.* (Standard test methods for analysis of Fluorspar is presented in Appendix 2.)

- *The primary concern to the consumer will be the very fine particle size of the product. It would be essential for standard HF plants to be modified with tailor-made fine particle handling and dust controls before this product could be used.*

- *By integrating the Moina operation as the exclusive supplier to the existing aluminium and fluoro-chemical industries in Australia, these industries would gain a long-term secure non-Chinese non-developing country source of raw material. This strategy would lead to an economic edge over their competitors and an economic benefit to Australia as a whole. Moreover, the price of fluorspar is currently at a historical high while stocks are at a historical low.*

- *There would be no abnormal complications with the processing flowsheet, but operating costs would be unusually high due to the need for very fine grinding.*

- *Moina fluorspar would carry the advantages of no* P_20_5*, arsenic, or lead and a low sulphur content, but would suffer the disadvantages of high* Fe_3O_4 *and* SiO_2 *contents and, most importantly, a very fine particle size.*

- *The option of processing the ore to metallurgical grade fluorspar is fatally flawed. Due to the intimate association of the fluorite with silicates, it would be impossible to reach the necessary 60 effective* CaF_2 *units without fine grinding, flotation, and briquetting. These are high operating cost processes which would make the product uncompetitive and uneconomic. Moreover, metallurgical grade viability* *will not improve with the passing time due to the progressively diminishing and progressively more environmentally-sensitive end use.*

- *While the benefit from the other economic minerals will be significant due to their high prices, their recoveries will be limited. Cassiterite recovery by gravity separation will likely be less than 20% and the grade poor, and some of the past testwork indicates that any recovery at all may be optimistic. However cassiterite flotation was not tested and this method of separation is likely to provide the highest recovery. The recovery of the scheelite is likely to be less than 70%, and, although the recovery of the sulphides (with gold) should be higher, estimated at 70% to 80%, the grade is likely to be lower than standard. A magnetite-rich concentrate will be recovered, and there is a possibility of recovering further magnetite from the flotation tailings. However the resulting SG is unknown, putting magnetite marketability and value for heavy media uses in doubt. The particle size of the garnet would meet only the finest ANSI polishing grade specifications, and as this represents a speciality market only, the garnet will not contribute significantly to the revenue of the project.*

- *The inferred resource of 26.5 Mt at 18%* CaF_2 *would be sufficient to sustain an output of 180,000 t/y of fluorspar filtercake for at least 21 years from the Comalco area, and this life would be extended using the resources known to exist but not measured in the immediately surrounding areas.*

- *The geographic location, pre-existing infrastructure and facilities, and shallow deposit at Moina carry competitive advantages over many alternative sources of fluorspar from currently proposed new projects.*

- *Moina is outside the nearby environmentally sensitive areas and there should be no restrictions preventing development of the project, and the availability of plentiful supplies of soft fresh water is a particular benefit for fluorspar processing.*

5. TUNGSTEN – WOLFRAM BERGBAU AND METALLURGICAL TESTWORK

At Moina, tungsten occurs as scheelite and, based on the assaying of drill core done to date by historic explorers and by Minemakers (refer Section 6), in situ tungsten, as tungstate, is about 0.1% in the skarn mineralization.

While at current prices this grade is insufficient for an economic stand-alone tungsten operation, the size and potential throughput of Moina indicates the possibility of significant tungsten output.

The original Comalco (pre-JORC) resource estimate was 24Mt, but this was for that part of the body with the least strip ratio. Based on the historic drilling, a resource of 50-60Mt may well be drilled out in the future. Taking this as a guide, Moina could be mined and processed at 3Mtpa with an annual production of 3,000t of tungstate on a 100% recovery basis. To put that into perspective, reference to Figure 3 indicates that this is almost 30% of current non-Chinese global tungsten production.

At its Rossarden properties, Minemakers has entered into an MOU with Wolfram Bergbau und Hutten-GmbH Nfg.KG ("Wolfram") which is anticipated will lead to a full Joint Venture. As part of it, Wolfram would be entitled to purchase any by-product tungsten from Minemakers' other Tasmanian operations, including Moina.

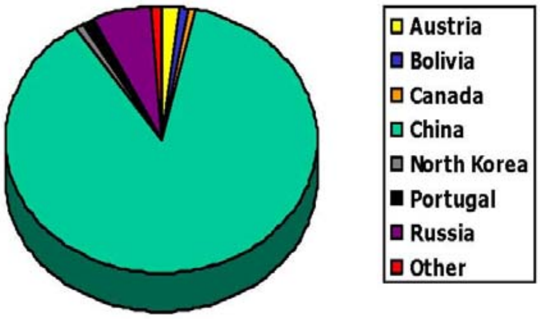
Wolfram is Europe's largest producer of tungsten from its mine at Mittersill in Austria, and is Europe's largest producer of tungsten carbide. Its mine supplies only about 20% of its tungsten needs. It has a metallurgical laboratory at Mittersill.

As scheelite would potentially be recoverable by flotation, as would both fluorspar and sulphides, Wolfram has agreed to undertake a flotation testwork programme on all three components. Delta has provided a flowchart showing the required work for the fluorspar, and this is presented as Appendix 3.

Testwork began in late August 2007 and initial results, at least, are anticipated by year end.

FIGURE 3 TUNGSTEN WORLD PRODUCTION 2006

	t
AUSTRIA	1,350
BOLIVIA	500
CANADA	700
CHINA	61,000
NORTH KOREA	600
PORTUGAL	800
RUSSIA	4,400
OTHER	700
TOTAL	70,000 t



NB: TOTAL CHINESE EXPORTS OF ALL TUNGSTEN PRODUCTS LIMITED TO 16,300t IN 2005. HENCE REST OF WORLD ONLY HAD ACCESS TO 24,000t OF TUNGSTEN PRODUCTS.

6. INFILL ASSAYING

As historic exploration had been directed at the particular commodity of interest to the various previous explorers, assaying of drill core has been inconsistent with respect to elements assayed. In particular, there was a relative paucity of assays for elements other than fluorine.

Minemakers recovered and split core held by MRT and had it infill assayed for W, Sn, Ag, Cu, Pb, Sn, Mo, Bi and Au.

185 @ 2m samples were assayed in this first infill effort. The assays have been incorporated into the database.

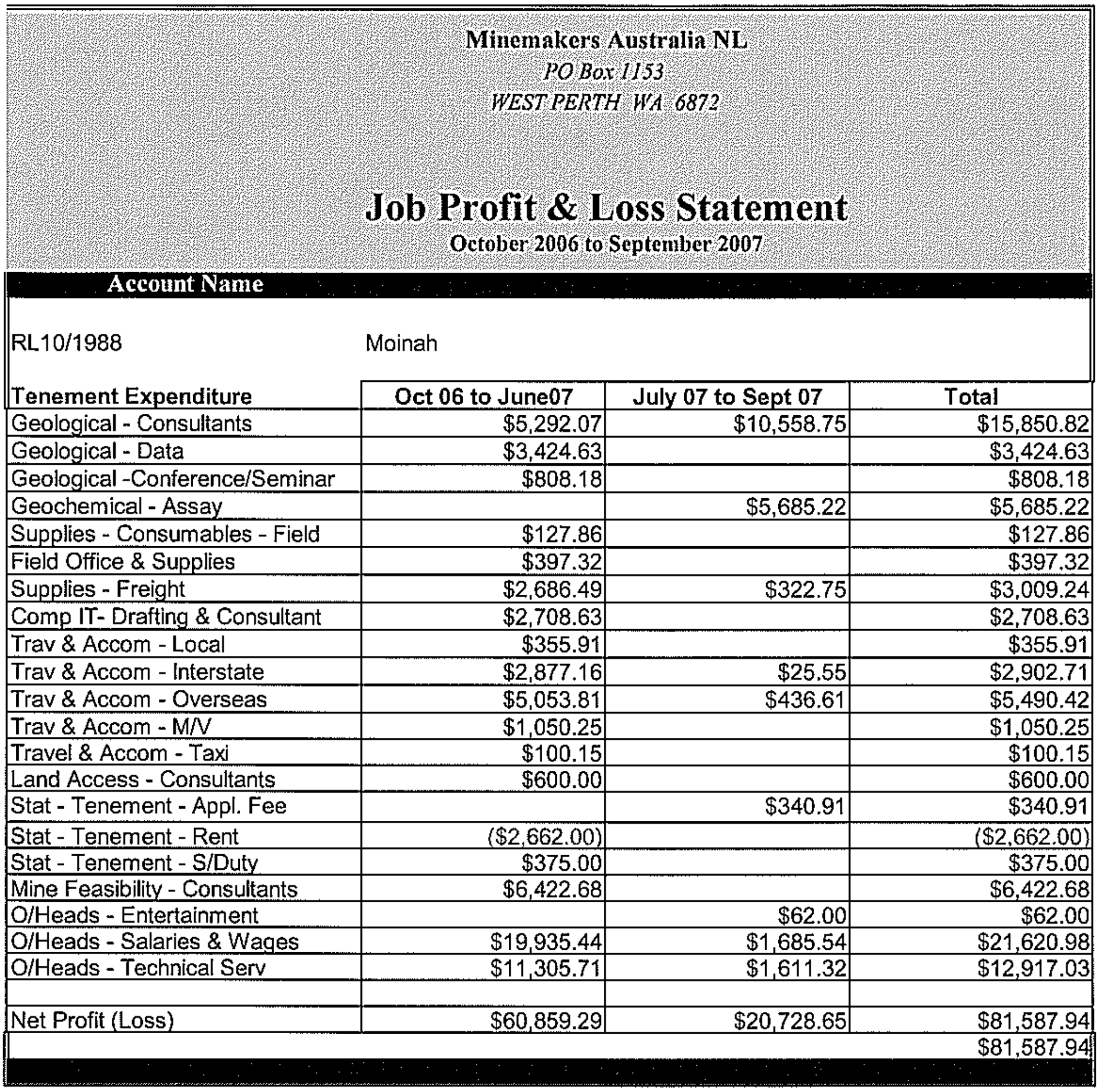
7. DATABASE

All historic and new data has been incorporated into a GIS database, using Perth-based contractors rOREdata.

That database is presented as Appendix 4.

8. EXPENDITURE

In the year under consideration, expenditure was $81,588 as shown on the Minemakers Job Profit & Loss Statement.



Minemakers Australia NL
PO Box 1153
WEST PERTH WA 6872

Job Profit & Loss Statement

October 2006 to September 2007

Account Name

RL10/1988 Moinah

Tenement Expenditure	**Oct 06 to June07**	**July 07 to Sept 07**	**Total**
Geological - Consultants	$5,292.07	$10,558.75	$15,850.82
Geological - Data	$3,424.63		$3,424.63
Geological -Conference/Seminar	$808.18		$808.18
Geochemical - Assay		$5,685.22	$5,685.22
Supplies - Consumables - Field	$127.86		$127.86
Field Office & Supplies	$397.32		$397.32
Supplies - Freight	$2,686.49	$322.75	$3,009.24
Comp IT- Drafting & Consultant	$2,708.63		$2,708.63
Trav & Accom - Local	$355.91		$355.91
Trav & Accom - Interstate	$2,877.16	$25.55	$2,902.71
Trav & Accom - Overseas	$5,053.81	$436.61	$5,490.42
Trav & Accom - M/V	$1,050.25		$1,050.25
Travel & Accom - Taxi	$100.15		$100.15
Land Access - Consultants	$600.00		$600.00
Stat - Tenement - Appl. Fee		$340.91	$340.91
Stat - Tenement - Rent	($2,662.00)		($2,662.00)
Stat - Tenement - S/Duty	$375.00		$375.00
Mine Feasibility - Consultants	$6,422.68		$6,422.68
O/Heads - Entertainment		$62.00	$62.00
O/Heads - Salaries & Wages	$19,935.44	$1,685.54	$21,620.98
O/Heads - Technical Serv	$11,305.71	$1,611.32	$12,917.03
Net Profit (Loss)	$60,859.29	$20,728.65	$81,587.94
			$81,587.94

APPENDIX 1:
DELTA MINERALS PTY LTD, JUNE 2007 –
THE POTENTIAL TO PROCESS MOINA ORE

MINEMAKERS LIMITED

MOINA PROJECT
TASMANIA

PRELIMINARY REVIEW

THE POTENTIAL TO PROCESS MOINA ORE

Report I
February 2007
Final Edition June 2007

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1.0 INTRODUCTION

Minemakers Limited has secured the title for the Moina multi-mineral deposit close to Bismuth Creek in northern Tasmania. The mineralisation was first discovered over 30 years ago in 1974, but despite extensive exploration of the licence area and confirmation of a substantial orebody containing fluorspar, magnetite, scheelite, tin, copper, zinc, bismuth, molybdenum, gold, and garnet, there has been no development beyond the exploration stage. The primary reason for the decision not to exploit the deposit originates from processing uncertainties. The ten potentially valuable minerals in the ore are closely associated in a fine-grained skarn and preliminary processing testwork in the 1970s on drill core samples revealed that poor recoveries and grades were obtained when attempting the separate the economic minerals from the gangue and the values from each other. As mineral processing technology has advanced significantly since the 1970s both in terms of efficiency and reduced cost, and the value of fluorspar and tungsten have increased dramatically in recent years, Minemakers has commissioned Delta Minerals Limited to study the historical fluorspar-related data with a view to forming an opinion whether this ore can be economically processed to produce acidgrade fluorspar at a marketable specification. This opinion will then be used to decide the most suitable route to adopt to advance the project to the next stages in the development of a multi-mineral mining and processing operation. Should the opinion be negative for acidgrade fluorspar production, then the alternative possibility of producing metallurgical grade fluorspar will also be examined. While taking into account all the other economic minerals, this review will focus on the potential of the fluorspar.

2.0 BACKGROUND

The exploration licence for the Moina area was first granted to Comalco Ltd in July 1974. Comalco's objective was to locate and develop a fluorspar orebody which would provide an in-house source of raw material for aluminium fluoride production to satisfy the needs of its aluminium smelting operations. Over the following two years, the licence was successively extended until the Moina area was defined to include the Shepherd and Murphy area, the Iris River area, the Lea River area, and the Black Buff to Smith Plains area. After adding the Mayberry area and the Oliver's Hill area, the total catchment of the licence reached 488 km^2 by November 1976.

Comalco carried out extensive exploration and investigation work over the entire area and, by May 1980, they drew the conclusion that the main resource of valuable mineralisation lay in a small target zone forming the Shepherd & Murphy and immediately surrounding area. In May 1980 the joint-venture, Comalco/Shell Company of Australia Ltd continued evaluating the extent of the deposit in the narrowed Comalco target zone and collected drill core samples for mineralogical analysis and processing testwork. In October 1988, a new licence was granted to the newly-formed joint-venture between Shell Company of Australia Ltd and CRA Exploration Pty Ltd for an area of 2 km^2, referred to from then onwards as the Comalco area or the extended Shepherd & Murphy area. It is the extensive data accumulated for this area which is the focus of this report.

Over the period between 1974 and 1991, five comprehensive reports with associated correspondence and extensive appended data and one published paper were written to summarise the progress of the exploration and investigations. The sections of these reports and correspondence which apply to the Comalco area comprise the data now under review for an opinion of the potential of the deposit as a viable future source of acidgrade fluorspar for both the Australian and international markets.

3.0 SCOPE AND OBJECTIVES TO BE MET BY THE REVIEW

3.1 MISSION

Delta Minerals was invited by Minemakers to undertake a review of the existing data with a specific mission to identify any already known characteristics of the Moina deposit in the Comalco area which would prevent the processing of the ore into a fluorspar concentrate of internationally acceptable specification and associated by-product concentrates of the other valuable minerals. Assuming that the beneficiation of the ore was not found to be technically or economically fatally flawed, the review would outline a suggested schematic processing route and recommend the next stages to be undertaken in the development of the project.

3.2 OBJECTIVES

3.2.1 Primary Objectives

These were agreed as follows:

- To evaluate the amenability of the ore for beneficiation to an acidgrade concentrate at internationally accepted specifications and form an opinion concerning any potential pitfalls.
- To highlight the potential for revenue streams from by-products, including scheelite, cassiterite, base metal sulphides, magnetite, and garnet concentrates, but excluding the evaluation of the processing of these minerals in detail.
- To suggest a possible processing route for fluorspar and illustrate this with an exploratory schematic flowsheet.
- To reveal the predicted benefits and any potential complications that are likely to be experienced while processing the ore.
- To highlight recent developments in processing technology with direct relevance to this ore.

- To recommend the next stage to be undertaken in the development of the project and, assuming the project is not flawed, to outline the scope of a preliminary evaluation programme leading to a pre-feasibility study.
- To identify and recommend an appropriate role for Delta Minerals in the future development stages of the project.

3.2.2 Secondary Objectives

In the event that beneficiation of the ore to acidgrade specification is flawed and unlikely to proceed, the review will substitute the assessment of acidgrade fluorspar production with:

- Evaluation of the ore for producing a metallurgical grade product at internationally recognised specifications.
- Recommendations for specific areas of focus for processing research work or further mineralogical studies to address the flaws identified.

3.3 SOURCES OF DATA

The following data from the extensive Comalco and Shell/CRA exploration work and subsequent investigations was made available for this review. In addition to the reports themselves, comprehensive appendices and associated correspondence were included with the reports:

1. Moina – Exploration and Investigations to September 1978, by PW Askins, September 1978;
2. Update Report on All Investigations to August 1979, by PW Askins, August 1979;
3. Update Report on the Shepherd & Murphy Area, by PW Askins, May 1980;
4. Geology and Genesis of the F-Sn-W Skarn (Wrigglite) at Moina, by PW Askins & TAP Kwak, Economic Geology, Vol 76, 1981, pp 439-467;

5. Progress Report on Exploration during the Period 1/1/80 to 31/7/81, WD Smyth, 25 September 1981;
6. Supporting Data to Accompany Application for Retention Licence over the Moina Wrigglite Skarn, 18 May 1987;
7. Moina Joint Venture – 1991 Annual Status Report, JP Randell, September 1991;

3.4 CONFIDENTIALITY

The data received and reviewed during this study, and this review report, are the property of Minemakers and will remain strictly confidential between Minemakers and Delta Minerals unless specifically placed in the public domain by Minemakers.

4.0 BRIEF SUMMARY OF DATA

4.1 GEOLOGY AND MINERALOGY

The Moina area is known for its tungsten and tin mining history. Complex Cambrian acid volcanics, pyroclastics, and clastic rocks are overlain by Ovdovician Roland conglomerate, Moina sandstone, and Gordon limestone. The fluorite skarns in the area are metasomatic replacements of the Gordon limestone. The main skarn zones have formed adjacent to faulted and fractured areas where the faults have acted as conduits feeding mineralising fluids into the limestone from the Dolcoath granite below. Along the alignment of the largest fault, the Bismuth Creek fault, skarn formation is greatest in the area of the former Shepherd & Murphy mine, and it is this area which will be the centre of attention for this review. In the past, vein type deposits in a quartz gangue were worked for tin, tungsten, galena and gold. All the veins were small, including those at the Shepherd & Murphy area, where the veins were in the range 200 mm to 500 mm in width and up to 400 m long. Although minor bismuth and gold bearing areas are present in the skarn, the most significant mineralisation in the skarn is fluorite. The veins occur partly in the Moina sandstone and partly in the calc-silicate rocks and to a lesser extent pass into skarn with uniform width and composition throughout. The calc-silicate rocks vary in composition depending on the degree of metasomatic alteration in the transition zone between the Moina sandstone and the Gordon limestone. The main mineral constituents of this zone are pink/brown garnet and buff/green pyroxene. There are several variations to the skarn occurring in the area including a pyrrhotite-rich skarn, a spalerite-rich skarn, and a chlorite-rich skarn, but the main type is the fluorite-magnetite skarn. This latter type has a characteristic fine-grained and rhythmically fine layered contorted texture, appropriately named "wrigglite" by the Comalco exploration team. Since the primary source of fluorspar in the entire region is in the wrigglite located in the vicinity of the Comalco area, the processing flowsheet will be developed on the basis of Comalco area wrigglite ore feeding the plant.

4.2 WRIGGLITE MINERALOGY

4.2.1 Texture

The distinctive rhythmically finely layered contorted texture is illustrated in the three slides shown in Photo 4.2.1 below:

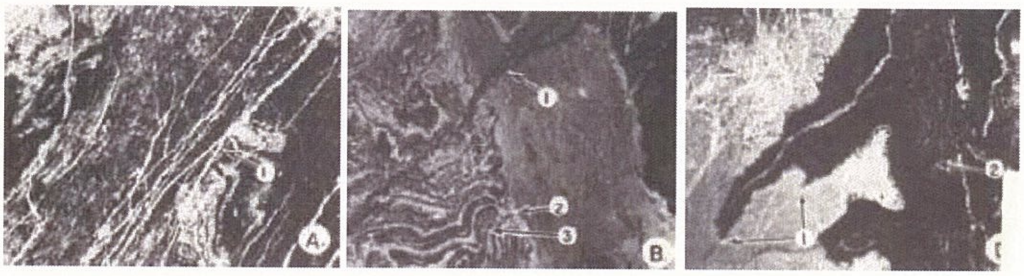


Photo 4.2.1

The grain size of the main constituents varies within a range of about 2 µm to 3 mm, and the mean grain size is too fine to see the constituent minerals with the naked eye or with a hand lens. On rough or freshly broken surfaces, especially when wet, the fine layered texture is almost invisible and the rock can easily be mistaken for basalt. The fine layers extend only a few centimetres before either circling back on themselves or being cut by other layers. The overall visual impression of a wrigglite outcrop is of a chaotic finely banded structure with contorted layered sequences and occasional pipe-like concentric swirls.

4.2.2 Mineralogy

In thin section, the wrigglite is fine-grained and complex. The main constituents are magnetite, fluorite, and a variety of silicate minerals. The primary silicate minerals are feldspar, sericite, ferrohastingsite, green biotite, andradite garnet, diopside, and idocrase. Pyrite, chalcopyrite, marcasite, and sphalerite are abundant in places. The minor minerals with economic significance include very fine cassiterite, fine scheelite, fine bismuthinite, and sphalerite in some zones.

The fine grain size and interlocking of the valuable minerals is of great relevance to the success and efficiency of the beneficiation process. Consequently four separate samples of wrigglite representing the extended Shepherd & Murphy zone were collected for detailed mineralogical examination. One polished section and four thin sections were prepared from each sample, making 20 sub-samples in total. The mineralogical characteristics of each of the valuable minerals is summarised in the following sections:

4.2.2.1 Fluorite

All samples revealed that the fluorite was very fine, generally less than 50 µm and rarely exceeding 100 to 200 µm. Where it occurs in the infrequent coarsely crystalline patches and veinlets, it attains sizes up to 500 to 600 µm and can be fairly free of interlocking with other minerals. However this is not the norm, and the fluorite is generally intimately intergrown with other minerals, mainly magnetite but also a variety of silicates such as feldspars, micas, diopside, ferrohastingsite, and others. Stringer veinlets of quartz-fluorite and adularia-fluorite, andesine-fluorite, and muscovite-quartz-fluorite-oligoclase are common in places. Individual crystals and crystal aggregates are rarely seen together; most crystals occur as individuals, interspersed with and isolated by other minerals. The fluorite is usually clear and colourless or pale purple, and only very occasionally strongly coloured.

4.2.2.2 Scheelite

In contrast with fluorite, the scheelite is coarser-grained, in the range 20 to 300 µm, extending up to 700 µm maximum. It is consistently if not exclusively associated with late-stage feldspar-fluorite veins which tend to be pinkish in colour, and occurs as irregular and anhedral grains. There was no evidence of intergrowth with feldspar. This scheelite fluoresces blue and white under UV light suggesting low molybdenum content, unlike scheelite with and higher molybdenum content which fluoresces yellow.

4.2.2.3 Cassiterite

This mineral is distributed widely in very small amounts in all the rock types. However, due to its very fine grain size in the range 5 to 50 µm (occasionally up to 100 µm max), it is difficult to detect. Intergrowth with fluorite, quartz, and feldspars is common.

4.2.2.4 Magnetite

Magnetite occurs mainly as thin bands of very fine individual crystals in the range 2 to 100 µm, with most crystals being about 20 µm, and also as aggregates of fine crystals. Intimate intergrowth with fluorite is common and magnetite also forms very thin films and shells up to 5 µm in thickness around other minerals.

4.2.2.5 Sulphides

With the exception of pyrite, sphalerite is the most abundant sulphide, but is erratic in its distribution and is often intergrown with magnetite. Again, the grain size is generally very fine at less than 50 µm, although semi-continuous patches also occur. Fine-grained bismuthinite was present in all samples at less than 20 µm. Chalcopyrite was observed as irregular patches up to 100 µm across, and molybdenite was detected as sporadic small flakes.

4.2.3 Effects of Mineralogy on Beneficiation

It is without doubt that the fine grain size and common small-scale intergrowths will increase the complexity of processing and will prevent high recoveries of all the economic minerals. Of particular importance is the influence of the grain size and the intergrowths on the processing of fluorite. In addition to poor recovery, there is a greatly elevated risk that high impurity levels in the final acidgrade concentrate may result in the product failing to meet international specifications. The primary concern is the presence of fine magnetite and silicate intergrowths which may need to be either rejected or diverted into a low-grade by-product in order to ensure that the acidgrade product complies with market requirements. Alternatively, there may be a need to restrict the market for Moina fluorspar exclusively to consumers who are prepared to modify and tune their plants to accommodate a sub-acidgrade concentrate, as occurs widely in Russia. Of lesser concern, while being a potential source of revenue, the presence of fine grained sulphides raises the risk of the acidgrade concentrate failing to meet the stringent sulphide sulphur and total sulphur specifications.

On the positive side, the lack of any arsenopyrite, apatite, or lead oxides ensures that there are no risks of arsenic, phosphorous, or lead tainting the concentrate. These are particularly troublesome impurities which cause both technical and environmental problems for acidgrade fluorspar end users, and their absence is a strong marketing advantage. Unlike many fluorite skarns found elsewhere in the world, Moina wrigglite has only one fluorine-containing mineral, fluorite; the absence of fluorosilicates or magnesium fluoride minerals simplifies the processing flowsheet and reduces reagent operating costs.

4.2.4 Mineral Composition

In general terms, the mineral composition of Moina wrigglite can be summarised as mainly magnetite, fluorite, and silicates, with minor clays and carbonates, and very small amounts of scheelite, cassiterite, and sulphides. The density of wrigglite was found to be SG 3.3 t/m^3. This high density provides a useful tool for reducing costs through pre-concentration and subsequent rejection of any dilution rocks included with the ore during open pit mining. In view of the need for very fine grinding, pre-concentration would be a particularly attractive option, however initial indications are that it may not be required as the fluorite skarn is 20 to 100 m thick and fairly homogeneous throughout, and the black colour of the wrigglite is easily distinguished from the green-brown country rocks. In the case of the Moina deposit, the pre-concentration option is available should the selectivity of the open pit mining method/plan demand it.

As a guide for processing testwork and for developing a processing flowsheet, the approximate mineral composition has been calculated from the chemical compositions in Table 4.2.5 and is shown in Table 4.2.4:

General Mineral Composition of Moina Wrigglite
Table 4.2.4

Description	Composition Calculated as:	%
Magnetite	Fe_3O_4	28.5
Fluorite	CaF_2	20.3
Silicates	SiO_2	24.2
Carbonates	$CaCO_3$	12.0
Scheelite	WO_3	0.18
Cassiterite	SnO_2	0.28

4.2.5 Chemical Composition

A bulk composite sample of Moina wrigglite from dumps in the Shepherd & Murphy area and thought to be fully representative of the underlying deposit was analysed for key elements. The assays are shown in Table 4.2.5:

Chemical Composition of Moina Wrigglite
Table 4.2.5

Element	Assay	Units
F	9.9	%
Ca	15.2	%
Si	11.3	%
Al	3.9	%
Fe	20.7	%
Mg	1.4	%
Cu	120	ppm
Pb	75	ppm
Zn	810	ppm
Ag	0.1	ppm
Au	0.035	ppm
Be	30	ppm
Sn	2250	ppm
W	1400	ppm
Bi	350	ppm
Mo	115	ppm
Sb	45	ppm

4.3 RESOURCES

Although the deposit has been extensively diamond-drilled, the spacing of the holes exceeds the standard set by the Australian Institute of Materials, Minerals and Mining for measured or indicated resources. However, the wrigglite tonnage calculation fully conforms with the standards set for inferred resources, and is summarised in Table 4.3:

Comalco Area Wrigglite Resource
Table 4.3

	Tonnes Mt	CaF_2 %	Sn %	WO_3 %	Stripping Ratio
Wrigglite	26.5	18	0.1	0.13	-
Overburden	8.5	-	-	-	3:1

The figures in Table 4.3 reveal Moina to be the leading fluorspar resource in Australia, containing over five times more fluorspar than the next largest resource, and with the benefit of possible tin, tungsten, and magnetite by-products.

5.0 FLUORSPAR SPECIFICATIONS

Traditionally there have been three grades of fluorspar traded on the international market – acid, ceramic, and metallurgical. Specifications for acidgrade and metallurgical grade are well-defined, although the requirements set by individual consumers may vary, especially in the areas of minor impurities and particle size.

5.1 ACIDGRADE FLUORSPAR

Acidgrade fluorspar is defined as containing more than 97% CaF_2, but some manufacturers of hydrofluoric acid, both in the United States and in Europe, are able to use discounted 96% CaF_2 fluorspar, or slightly lower, if the remaining impurities are acceptable to their particular plant and downstream products. At the lower extreme, the Russian specification for acidspar from Russian and Mongolian producers is set at not less than 92% CaF_2. Elsewhere in the world, the composition of the remaining 3% of non-CaF_2 components is of prime importance, and, because the specifications for the impurities within this 3% are so stringent, in practice acidgrade fluorspar must exceed 98% CaF_2 for most hydrofluoric acid markets and 98.5% CaF_2 for most aluminium fluoride markets. Different consumers specify different limits for these impurities, but broadly their specifications are summarised in Table 5.1a. The values for consumers who demand tight specs are shown in the left column while those for less demanding customers are shown on the right. These are the most stringent and most lenient specification limits for each assay currently applicable worldwide in 2007, however it must be emphasised that not all the quoted high or low assay limits apply to any single consumer. As a general rule, the price for a higher-spec product exceeds that of a lower-spec product, and there are some consumers who are who are prepared to take heavily discounted fluorspar which fails to meet their specification for one impurity on the basis that they will blend with another producer's non-discounted product which is very low in that impurity. In the case of fluorspar produced from Moina wrigglite, it is particularly important to appreciate that consumers specify a required particle size range as well as chemical analysis, and in many cases they also specify the method of analysis and analytical procedure to be used in both chemical and sizing analyses.

Range of High and Low Acidgrade Specifications For Major Consumers
Table 5.1a

Assay	Unit	Stringent Specification	Lenient Specification
CaF_2	%	> 98.5	> 97.0
SiO_2	%	< 0.4	< 1.0
$CaCO_3$	%	< 0.6	< 1.5
P_2O_5	ppm	< 150	< 2000
As	ppm	< 2	< 10
Total S	%	< 200	< 500
Sulphide S	ppm	< 25	< 700
Fe as Fe_2O_3	%	< 0.09	< 1.5
Al_2O_3	%	< 0.1	< 0.5
R_2O_3	%	< 0.5	< 1.5
MgO	%	< 0.1	< 0.1
$BaSO_4$	%	< 0.5	< 1.0
Cu	%	< 30	< 200
Pb	%	< 100	< 2500
Zn	%	< 20	< 200
Hg	ppm	< 0.1	< 1.0
Organics	%	0.015	< 0.1
Total Cl as NaCl	%	< 0.02	< 0.5
Soluble Cl as NaCl	ppm	< 20	< 50
H_2O	%	< 10.0	<10.0

Where acidgrade is specified dry, the maximum moisture is usually 0.1% H_2O.

Range of Fine and Coarse Particle Size Specifications For Major Consumers
Table 5.1b

Mesh	Microns	Fine Specification Cum % Passing	Coarse Specification Cum. % Passing
100	150	> 95	> 80
200	75	> 75	> 60
325	45	< 60	< 45
-	5	< 5	< 5

5.2 CERAMIC GRADE FLUORSPAR

The use of ceramic grade fluorspar has declined worldwide, especially in the United States and Europe where the main former markets were, but it is still offered by some suppliers. Unlike acidgrade, ceramic grade has no precise definition, but there are basically two grades, Ceramic No. 1, containing 90% to 95% CaF_2, and Ceramic No. 2, containing 85% to 90% CaF_2. In recent years, progressively tightening environmental regulation has placed restrictions on the emissions of the impurities with the result that many former consumers of ceramic grade now use acidgrade. Some fluorspar suppliers, whether they be producers, traders or merchant processors, still offer ceramic grade, but because practically every ceramic grade user sets his own specifications according to local regulations, suppliers tailor their products accordingly or offer several product grades that fall across the range between metallurgical grade and acidgrade. In addition to the CaF_2 content, ceramic grade customers specify limits on SiO_2, $CaCO_3$, P_2O_5, Fe_2O_3, As, Pb, Zn, and sulphur. Ceramic grade is generally supplied as a dried concentrate with 0.10% H_2O, but for some ceramic uses up to 1% or 2% is required to prevent dust generation.

Due to the small and steadily diminishing market for ceramic grade, which is insufficient to adsorb the scale of production proposed for Moina, this study will not dwell any further on ceramic grade.

5.3 METALLURGICAL GRADE FLUORSPAR

Although more accurately defined than ceramic grade, the specifications for metallurgical grade vary from country to country and from one end user to another. In the United States, metallurgical grade fluorspar contains a minimum of 80% CaF_2 and can reach as high as 93% CaF_2. The primary function of metallurgical grade fluorspar in the steel industry is as a flux, and consequently silica and silicate impurities are of concern as they negate the fluxing properties of the fluorspar. The quality of metallurgical grade is determined by its effectiveness as a flux and is measured in effective units. The effective units are calculated by multiplying the

SiO_2 content by 2.5 and subtracting the result from the CaF_2 content. In addition to silica, the specification for metallurgical grade sets impurity limits for the content of $CaCO_3$, Pb, and sulphur, and, of equal importance, upper and lower particle size limits are specified.

Range of High and Low Metallurgical Grade Fluorspar Specifications
Table 5.3a

Assay/Particle Size	Unit	Stringent Specification	Lenient Specification
Effective Units	-	> 60	-
CaF_2	%	-	> 75.0
SiO_2	%	-	< 15.0
$CaCO_3$	%	< 9.0	< 10.0
Pb	%	< 0.5	< 0.8
Total S	%	< 0.3	< 0.5
Passing 63 mm (2½")	%	100.0	> 99.0
Passing 10 mm (⅜")	%	< 15.0	< 20.0

The lower particle size limit is particularly relevant to Moina wrigglite. In view of the 20% CaF_2 and 24% SiO_2 content and the intimate association between CaF_2 and SiO_2 minerals, it is most unlikely that a metallurgical grade quality of 60 effective units could be achieved without reducing the particle size far below the minimum limit of 15% passing 10 mm. One possible but rather expensive remedy to this problem would be to concentrate the CaF_2 to metallurgical specification at a finer particle size, then briquette the concentrate to meet the minimum size spec. In the past there was significant usage of metallurgical fluorspar as briquettes in the steel industry, but with the marked decrease in CaF_2 consumption by the steel industry especially in the US and Europe, this practice is no longer widespread. There is sufficient on-spec metallurgical grade gravel available worldwide to satisfy the diminishing markets, thus removing any justification to briquette fine concentrates. The few remaining briquette producers specialise in bespoke formulations for specific customers requiring the metallurgical fluorspar to be combined with other fluxing materials such as lime which would otherwise be difficult to feed into the furnace. Due to the brittle nature of briquettes, multiple handling during shipping causes the re-generation of fines, and as a consequence briquetters tend to be located geographically close to the consuming steel plants.

6.0 PROCESSING MOINA WRIGGLITE

Exploratory metallurgical testwork in the early stages of the Moina project revealed that wriggleite was difficult to treat by flotation. In 1976, investigations into leaching and research into a potential new ammonium sulphate roasting process were undertaken by The Australian Mineral Development Laboratories (Amdel). As the results concluded that the alternatives were uneconomic, Amdel was then requested by Comalco in 1977 to study the physical beneficiation of Moina wrigglite in sufficient detail to make an unequivocal decision over the economics of producing an acidgrade concentrate from wrigglite.

There were three objectives:

- To produce an acidgrade fluorspar concentrate at maximum recovery;
- To produce a lower grade fluorspar concentrate suitable for leaching and/or roasting treatment; and
- To make separate scheelite, cassiterite, and magnetite concentrates.

6.1 SUMMARY OF PREVIOUS TESTWORK

6.1.1 Liberation Study

Using the combination of heavy liquids, size analyses, and mineralogical examination, the liberation sizes of each of the economic minerals was determined:

6.1.1.1 Fluorite

Liberation is about 80% complete in the size range – 17 + 9 μm. Unliberated fluorite is approximately equally locked with magnetite and silicates.

6.1.1.2 Cassiterite

Approximately 45% of the cassiterite is contained in solid solution in garnet. Less than 5% of the remaining cassiterite is liberated at sizes greater than 9 µm.

6.1.1.3 Scheelite

Scheelite is the only economic mineral which liberates at conventional flotation particle size. About 50% of the scheelite is free at – 150 + 75 µm, and most of the remaining middlings liberate in the range – 75 + 45 µm.

6.1.1.4 Magnetite

Magnetite is intimately associated with silicates and fluorite, and composites are abundant down to 5 µm.

6.1.1.5 Garnet

Garnet is in abundance but intimately associated with and locked to fluorite and magnetite down to 15 µm. In addition, some of the garnet contains cassiterite in solid solution. Due to the fine liberation size, the garnet will meet only the finest ANSI polishing grade specifications, and is unlikely to be of economic value outside this very small niche market.

6.1.2 Magnetic Separation

Due to the presence of magnetite/fluorite composites, magnetic separation was found to be an unsatisfactory means of removing magnetite, both prior to fluorspar flotation and from the cleaner concentrate. In both cases, despite a fine grind, the fluorite losses were excessive. At best, the magnetic fraction contained 24% CaF_2, while the non-magnetic fraction assayed 5.5% Fe.

6.1.3 Flotation Testwork

Grinding to 17 µm is a prerequisite for fluorite flotation, but scheelite can be separated prior to fluorite flotation. On the other hand, cassiterite was barely liberated above 9 µm and was below the minimum size limits for both gravity and flotation, thus the prospects of economic tin recovery are slim.

After only nine bench flotation tests, a 93.1% CaF_2 concentrate containing approximately 2.0% Fe_3O_4, 2.5% SiO_2, 1.0% $CaCO_3$, and 0.4% WO_3 at a recovery of 65% CaF_2 was achieved. Under these unusually complex liberation circumstances, this is a commendable result. The concentrate was produced after primary grinding and conventional rougher and scavenger flotation followed by regrinding and 6-stage conventional cleaning. This was an open cycle test and none of the 29% CaF_2 distribution in the cleaner tailings products was apportioned to the final recovery. In a locked cycle test, there would be an improvement of the 65% CaF_2 recovery achieved. The flotation conditions, the reagent types, and the quantities added were consistent with industry practice at the time. However it is important to note that none of the flotation conditions were optimised, and the report issued at the time emphasised that optimisation would lead to an 'overall improvement in flotation response'.

6.1.4 Roasting Treatment

Amdel also carried out a research project to investigate the possibility of by-passing the physical beneficiation stage which relies on liberation, by subjecting the crushed and dry-ground wrigglite ore to a purpose-made ammonium sulphate roasting process. This is a relatively low temperature roast, where the dry-ground ore is mixed with ammonium sulphate and heated in a kiln to about 400°C for about two hours. At this temperature a series of reactions take place where all the products are gaseous, other than calcium sulphate waste and the residual gangue from the ore. The hot gases were collected, and after a series of adsorption and scrubbing stages, HF was collected and condensed. While this new roasting process appeared to present the ideal solution to the physical beneficiation problems, it had one major flaw: the ammonium sulphate was also consumed by the magnetite with the consequence that the consumption of high-cost ammonium sulphate was excessive. The only route to success for this new process was for the ore to be first prepared by fine grinding and flotation to remove the magnetite, and then the dried concentrate would be fed into the new process. However, by requiring a pre-flotation stage, there was no need for the new roasting process, as the flotation concentrate could be used to produce HF by the conventional lower-cost H_2SO_4 reduction process. The concept was therefore a non-starter and the research was terminated.

6.1.5 Pyrohydrolysis Testwork

Further research was undertaken into another non-commercial treatment route. Ore was crushed to 10 mm and heated in the presence of steam to 1,300°C for up to four hours. Unlike other processes where SiO_2 is a disadvantage, this process relies on the presence of SiO_2 to produce $CaSiO_3$ and HF. Although the raw material costs of this process were low, the extremely corrosive nature and high temperature of the gases in the reactor made the engineering of the reactor impractical on a commercial scale. This research project was also discontinued.

6.1.6 Gravity Testwork

The Department of Mines in Tasmania completed a gravity testwork programme with the aim of recovering scheelite and possibly some cassiterite and base metal sulphides as by-products. They concluded that after grinding to 53 µm, only 33% of the scheelite was recoverable and the grade achieved was just 23% WO_3. Furthermore they concluded that 54% of the scheelite was not recoverable and none of the cassiterite was recoverable by gravity techniques. Further gravity testwork was abandoned. These conclusions are in conflict with the Comalco and Amdel liberation results which indicated that 50% of the scheelite is free at – 150 + 75 µm, and most of the remaining middlings become liberated in the range – 75 + 45 µm.

6.1.7 Conclusions Reached from Previous Testwork

- With the exception of scheelite which was mainly liberated at 75 µm, the other economic minerals were intimately associated with silicates and with each other to the extent that grinding to at least < 17 µm is essential for liberation.
- After fine grinding, a fluorspar concentrate assaying 93.1% CaF_2, and approximately 2.0% Fe_3O_4, 3.0% SiO_2, 1.0% $CaCO_3$, and 0.4% WO_3 was produced with a recovery of 65% CaF_2 from a composite feed sample assaying 16.5% CaF_2.
- Magnetic separation in a position either before or after fluorspar flotation was considered unworkable for the removal of magnetite due to unacceptable fluorspar losses.
- The primary contaminants and contributors to the sub-acidgrade final fluorspar flotation concentrate were magnetite, amphibole silicate, calcite, and scheelite. It was concluded that these impurities could be reduced with further flotation testwork.
- It was felt unlikely that an economic high-grade magnetite concentrate could be produced from this ore.
- Although the composite sample of wrigglite contained 0.13% Sn, 45% of this was locked in solid solution in garnet and was not recoverable tin. The remaining 65% of the tin was too finely disseminated (< 5 µm) for physical beneficiation.
- The Department of Mines in Tasmania concluded that only 33% of the scheelite was recoverable at a maximum grade of 23% WO_3, however previous Comalco mineralogical studies indicated that scheelite recovery should be much higher. Amdel did not attempt any scheelite gravity separation.

Given that all the exploratory physical processing testwork failed to produce acidgrade fluorspar at any recovery, that the very fine particle size would preclude sales to the international market even if grade improvements could be achieved, and that the exploratory roasting and pyrohydrolysis direct routes to produce HF were not economically viable, all further processing investigations were shelved and any further development of the deposit was brought to a halt.

6.2 ALTERNATIVE OPTIONS FOR PROCESSING MOINA WRIGGLITE

Regardless of the many improvements in processing technology since the 1970s, the underlying limitations set by the mineralogy of wrigglite still dictate the processing route. The ore will still need to be ground to < 17 µm for any type of physical separation of fluorite and the only workable option is flotation. Despite grinding to < 17 µm, economic recovery of cassiterite and magnetite is likely to be very poor if viable at all, and technology improvements since the 1970s will contribute only slightly. Gravity separation of the scheelite is most likely to give the highest grade and recovery, particularly in the size ranges greater than 53 µm where most of the scheelite should occur, according to the Comalco and Amdel liberation study. Selective flotation of scheelite from fluorite is possible, but when scaled up to a continuous process, re-circulating fluorite depressant destabilises the downstream fluorspar circuit causing lower than expected recoveries. The selective flotation route should be taken only if the gravity separation route fails. Recent improvements in reagent selectivity and equipment efficiency will enable fluorspar and sulphide concentrates to be produced, but the recoveries will be significantly lower than the industry norm and the grades will be sub-standard, placing the sale of the products and their value in world markets in question. If however the general mission of the project was diverted from aiming to supply the world market with acidgrade fluorspar to a specific objective to secure a long-term in-country source of fluorspar devoid of Chinese or developing country risk to the Australian aluminium and fluoro-chemical industries, then the potential of the wrigglite deposit becomes a realistic proposition. The underlying premise for this potential solution is that the HF plant/plants receiving the fluorspar from Moina will have to be specifically designed and geared to accept the very fine particle size of Moina fluorspar. The high levels of the two impurities, Fe_3O_4 and SiO_2 can be accommodated without technical complications. Once produced, HF from Moina fluorspar promises to be of high quality, suitable for AlF_3 manufacture and any of a wide array of downstream fluoro-chemical production options. The absence of P_2O_5, arsenic, lead, and chloride, and the low level of sulphur are highly attractive and exclude any of the technical difficulties that compromise many fluorspar concentrates available on the world market today even though they meet full acidgrade specification. While the geographically close in-country markets appear as the obvious choice for Moina fluorspar, there is no reason why Moina's markets need be in-country. Provided the end users have plants specifically adapted for a fine particle size feed, they could be located anywhere easily accessible by ocean freight.

6.2.1 Remaining Processing Options

Previous testwork and mineralogical studies have conclusively eliminated most processing options. There are just two unexplored possibilities:

- Processing to metallurgical grade fluorspar; or
- Processing to sub-acidgrade, assaying about 95% CaF_2.

6.2.1.1 Metallurgical Grade Option

Under normal circumstances, metallurgical grade fluorspar is produced in simple gravity treatment plants. The ore is crushed in primary and secondary circuits until all material passes through a 63 mm screen. In some operations the gangue liberation size requires crushing to 40 mm. The ore is then fed into gravity separators such as jigs or dense media drums where the separating density is set to about SG 2.9. After recycle of the dense media and removal of the water, the emerging final 'sink' stream will be the metallurgical fluorspar product. In the case of wrigglite however, firstly, due to the presence of magnetite, the SG of wrigglite exceeds the SG of fluorite (3.3 vs. 3.2 respectively), and secondly the particle size at which separation could be achieved is about 20 μm which is far below the 10 mm minimum limit for metallurgical grade. A gravity process is therefore a non-starter.

The alternative would be to crush and grind the ore to 20 μm removing as much of the scheelite as possible in an intermediate gravity stage en-route, then concentrate the fluorite by flotation. The objective would be to collect a 75% CaF_2 concentrate with 5% SiO_2 max with a high recovery. Previous testwork indicated that the recovery would be in the range 85% to 90% CaF_2. This product would also contain about 20% Fe_3O_4 which would not be a disadvantage to the steel manufacturing customer. However the flotation concentrate would have to be thickened, filtered, pelletised/briquetted, and cured to meet the strict particle size specification. These final stages together with the fine grinding stage involve high capital and high operating costs which would not be experienced by competitors supplying metallurgical grade gravel. Moreover, the price of metallurgical grade is US$80 to US$100 per tonne less than acidgrade, whereas processing costs by this route would be higher than for acidgrade. Production of metallurgical grade makes no sense and is very unlikely to be economically viable. This option should be abandoned.

For the record, it has been suggested that that there could be a possibility of producing a fluorite-rich magnetite product which would act as a "self-fluxing" iron ore. This option is unlikely to be realistic though final confirmation has not been sought. Even after pelletising or briquetting this specialised product, it may not carry any self-fluxing advantage as would first appear, and is unlikely to be attractive to the iron and steel maker. The normal fluxes added to the blast furnace in the first stage of iron making are limestone and dolomite, and sometimes lime. The limestone, $CaCO_3$, and dolomite, $CaMgCO_3$, form lime, CaO, and magnesia, MgO, respectively which then react with the acid components and impurities within the iron ore. These acidic minerals, mainly silica, SiO_2, and alumina, Al_2O_3, react to produce a fluid slag of lower density that separates and floats above the iron which is then tapped from below. Fluorspar is a neutral flux added at a later stage primarily to open-hearth steel making slags to improve their fluidity, but there is no clear reason for adding fluorspar to the blast furnace and this would be a non-standard procedure. Fluorspar is added to the slag in the cupola while holding pig-iron or steel products, again to maintain fluidity at the lowest possible temperature. If added to the primary blast furnace, fluorspar would reduce the viscosity of the slag which may or may not be useful, and this aspect would need further investigation. In addition, fluorspar in the blast furnace would add to the environmental complications of the operation as there would be a release of fluorine gas and other gaseous fluorinated compounds depending on the composition of the impurities in the iron ore. The "self-fluxing" route is therefore likely to be uneconomic and a non-starter.

6.2.1.2 Sub-Acidgrade

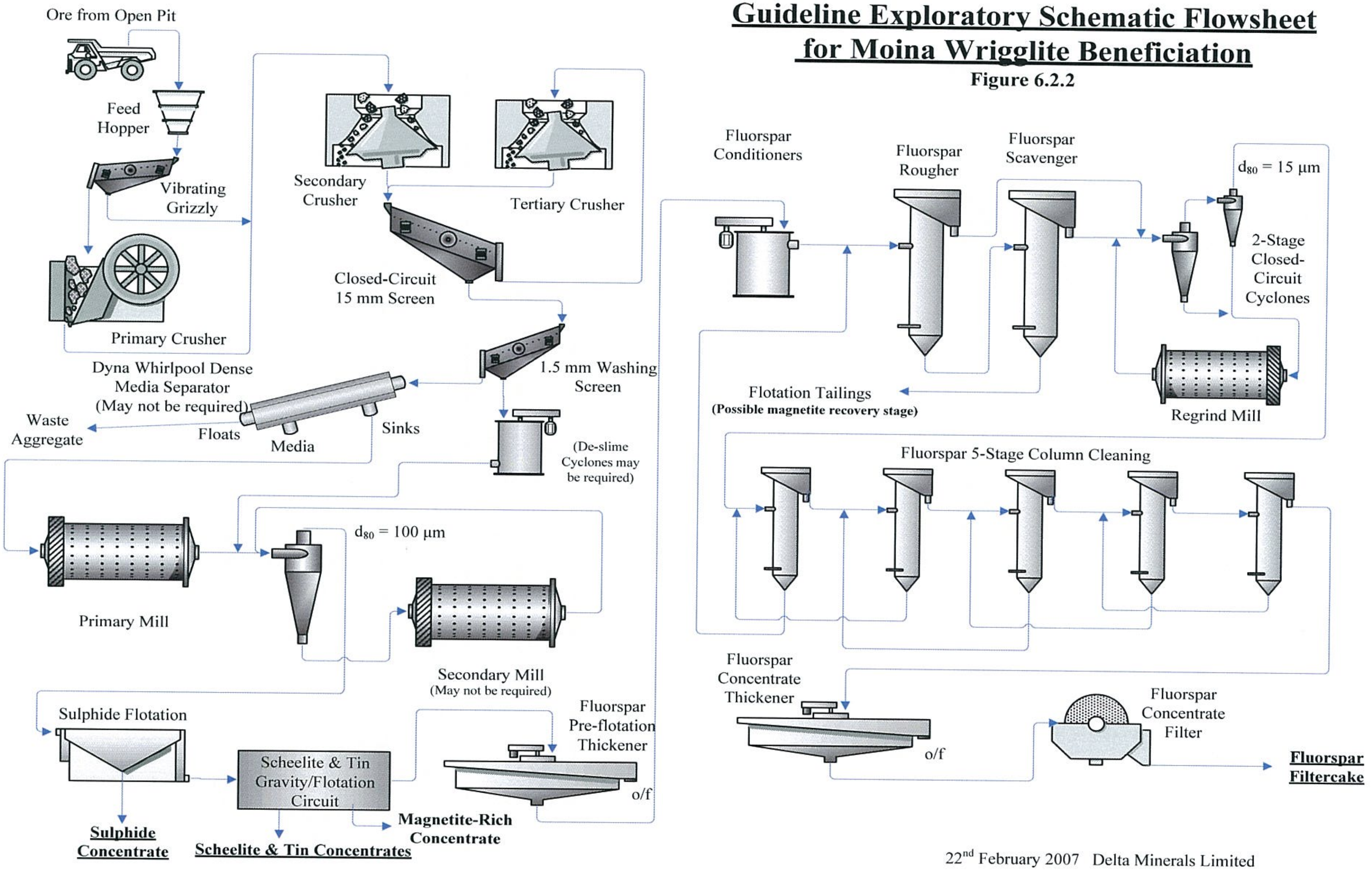
This is the only economic option. The ore would be mined in a conventional open pit and fed to a primary and secondary crushing plant. Should the mining plan require it, the option to reject non-wrigglite dilution in a pre-concentration plant is available. There may also be a need for a desliming circuit. From this point onwards, the composition of the ore can be considered to be similar to the wrigglite samples comprehensively examined by Comalco, i.e. roughly 20% CaF_2, 30% Fe_3O_4, 25% SiO_2, and 20% $CaCO_3$. Primary and secondary (secondary may not be required) grinding circuits would reduce the particle size to 80% passing 100 μm before introducing the slurry into a high-recovery bulk sulphide flotation circuit. Subject to the quantity and grade of concentrate collected, the bulk sulphide concentrate could be reground, separated into individual mineral concentrates, cleaned, thickened, and filtered. The bulk sulphide tailings would then go to a scheelite and cassiterite recovery circuit. Ideally this would be a gravity circuit which would also take out the free magnetite. The magnetite would subsequently be removed by magnetic separation leaving clean scheelite and cassiterite concentrates. Due to the liberation complication, the grade of the most of the magnetite concentrate may not meet the strict SG 4.6 minimum specification set for the higher value dense media market, consequently recovery of a saleable product may be low. There remains a possibility that fluorite losses in the gravity circuit may be unacceptable forcing scheelite removal by flotation. Similarly, the possibility of cassiterite flotation will need investigation as this is likely to lead to a higher recovery than gravity separation. The design and success of this circuit can only be determined empirically by undertaking further testwork. The flotation characteristics of scheelite and fluorite are similar making selectivity difficult to achieve and recovery poor, therefore flotation of scheelite would be a last resort. Having recovered the scheelite, the remaining pulp would be thickened prior to fluorite conditioning and flotation. The flotation conditions and reagent additions would be configured for a low-grade high-recovery column rougher and scavenger operation. The concentrate would be reground to 80% passing 15 μm in a 2-stage closed-circuit cyclone operation before being fed into a 5-stage column cleaner circuit. Dewatering and filtration of the resulting fine-sized concentrate will require a much larger thickener and filter than the industry norm. The filtercake product should well-exceed the grade achieved in the 1970s exploratory tests, and is very likely to reach an overall CaF_2 recovery in the range 70% to 75%. While difficult to predict at this very early stage, the final grade is likely to exceed 95% CaF_2, and contain less than 2.0% Fe_3O_4, 2.0% SiO_2, and 1.0% $CaCO_3$. These impurity levels can all be accommodated without difficulty by an HF/AlF_3 plant which is geared for this grade, but the very fine particle size will require specific modifications to the to the feed handling systems, and the pre-reactor, and a dust collection facility will need to be designed and fitted to prevent fine un-reacted fluorspar from being collected in the HF gas stream thereby short-circuiting the conversion reaction to HF and fouling subsequent stages. It is these factors which will limit the product to specifically tuned exclusive HF/AlF_3 markets. The only prospect for external trade will be to specific consumers who have also modified their HF plants correspondingly.

6.2.2 Guideline Schematic Flowsheet

A schematic flowsheet for the sub-acidgrade option is detailed in Figure 6.2.2. It must be emphasised that this flowsheet is designed to act as a guideline only. It is based only on the results of the 1970s tests and lacks any current supporting data.

Guideline Exploratory Schematic Flowsheet for Moina Wrigglite Beneficiation

Figure 6.2.2



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6.2.3 Metallurgical Advances since the 1970s Testwork

The main advances in fluorspar processing technology which are directly relevant to this project are:

- Introduction of column cells for fine particle size flotation;
- Improved selectivity of fluorspar flotation collectors;
- Improved selectivity of silicate and carbonate depressants;
- Improved flotation recovery through the use of a fluorspar activator;
- Major improvements in the efficiency of cassiterite flotation;
- Reduced energy consumption and improved recovery from flotation at ambient temperature;
- Improved understanding of the importance of reagent conditioning;
- Improved understanding of the influence of pH on flotation recovery and grade;
- Improved classification efficiency and throughput of cyclones with a fine particle size cut-point;
- Improved efficiency in dense media pre-concentration; and
- Improved efficiency in magnetic separation.

7.0 THE PROS AND CONS OF PROCEEDING WITH DEVELOPMENT

The deposit was extensively explored over a 20-year period in the 1970s and 1980s, and, despite the confirmation of large resources of wrigglite, the decision was taken to abandon all plans to develop the mine under the justification that processing of the ore to an acidgrade fluorspar quality product was not viable. This decision has been up-dated on several occasions since that time with the same outcome. Taking into account the availability and price of acidgrade fluorspar on the world market at that time, these decisions were fully justified. However, over the last four years fluorspar availability has progressively tightened and price has progressively risen. Over these few years, end users have been strategically planning to secure long-term sources of supply outside China for at least part of their annual requirement. In the last 12 months, their planning has turned to into action and strategic alliances or equity participation by consumers in producing operations have begun to emerge. In this context, Australia's aluminium and fluoro-chemical industry might wish to re-visit the possibility of participating in the development of an exclusive secure long-term in-country source of fluorspar. Should these industries wish to adopt this strategy and proceed with establishing Moina as their own secure source, then there is no reason why the capacity of the new Moina fluorspar operation should exactly match the fluorspar requirement for Australia's AlF_3/HF consumption. The value-added benefit of exporting excess-to-requirement AlF_3 and HF downstream products rather than exporting fluorspar would support the Australian economy as well as circumventing the problem of trying to market sub-acidgrade fluorspar elsewhere. The capacity of the fluorspar operation is beyond the scope of this study, however, as an example, the inferred resource of the deposit could sustain the following scenario:

Inferred Resource:	26.5 Mt @ 18% CaF_2;
Product Grade:	95% CaF_2;
Process Recovery:	75%;
Fluorspar Output:	180,000 t/y;
Downstream Production:	30,000 t of AlF_3 and 60,000 t of HF;
Mine Life:	21 years, using already-known inferred resource.

The key currently-known pros and cons which are central to the development of the Mina deposit are summarised and listed:

7.1 PROS

- A substantial inferred resource of 26.5 Mt @ 18% CaF_2;
- There is strong evidence from Comalco's exploration work in the 1970s that this inferred resource will increase significantly with additional drilling;
- The deposit is free from P_2O_5, arsenic, and lead minerals;
- Significant potential revenue contribution from scheelite, sulphides, and possibly cassiterite and magnetite;
- Shallow deposit suitable for low-cost open-pit mining, where the wrigglite extends from surface outcrops to a maximum depth of 150 m;
- There is a plentiful supply of fresh soft water suitable for fluorspar processing at the site, and no special precautions would be required for winter temperatures where the average high is 12°C and the average low is 5°C.
- There is a pre-existing in-country aluminium and fluoro-chemical industry;
- Moina lies about 50 km from the north coast of Tasmania and less than 100 km by road from the deep-water port of Burnie which is well-experienced in handling bulk concentrate shipments;
- Infrastructure and services in the Moina area already exist; access is via a main road to within a few kilometres from the site and electricity is already supplied to the area;
- Title to the deposit is secure and there are no developing country uncertainties;
- Tasmania has a mining history, consequently trained labour and specialised mining and maintenance services are already available;
- Although the Cradle Mountain Conservation Area is not far from the deposit, there are no environmental restrictions preventing development of a 1.5 Mt/y mining operation;
- The area is only very sparsely populated, therefore displacement and re-settlement difficulties would not arise;

7.2 CONS

- The complex mineralogy of wrigglite will limit the overall plant metallurgical recovery of fluorspar to the range 70% to 75%;
- The fluorspar grade will be sub-acidgrade, assaying about 95% CaF_2, and will be marketable only to consumers who have modified their plants to cater for the higher than usual SiO_2 and Fe content and the very fine particle size;
- Recovery of the other economic minerals will be low: scheelite probably less than 70%; base metal sulphides (with gold) possibly 80%; and the magnetite grade may not reach a specification sufficiently high for economic marketing. Tin recovery will probably be less than 20% and the garnet grade would meet only a very small niche-market specification if it can be marketed at all;
- The hard and abrasive ore combined with the need for an unusually fine grind will result in higher than normal operating costs especially in the area of energy consumption;
- The fine grind will cause high reagent consumption, further increasing operating costs;
- Dewatering the fine fluorspar concentrate will be technically challenging and will require higher than normal capital and operating costs.

While the sub-acidgrade quality of the fluorspar may give an initial impression that the project would be a non-starter, this assumption would only be correct if the product was destined for the international market. Provided Moina fluorspar is consumed only by HF/AlF_3 plants designed to receive this quality of product, then the project becomes a workable proposition. The entire Russian HF/AlF_3 industry is fed either with Russian, Mongolian, or Kazak fluorspar assaying between 93% and 96% CaF_2 or by $HSiF_6$ produced as a by-product from the fertiliser industry, and, because their plants are designed for this grade, they experience no problems.

8.0 RECOMMENDATIONS TO ADVANCE THE PROJECT

The success of the project hangs on the ability of the process plant to produce a 95% CaF_2 containing < 2.0 % SiO_2 and < 2.0% Fe_3O_4 at a recovery of 70% to 75% CaF_2. As this aspect is so critical, before soliciting funding for or committing to a pre-feasibility study, further exploratory flotation testwork is recommended.

The ageing of samples significantly influences sulphide flotation but rarely affects the performance of fluorspar flotation. Consequently, it would be feasible to carry out a further 20 to 30 bench flotation tests using a 50 kg representative composite sample from remaining 30-year old drill core logged during the Comalco drilling programme. These tests would have one objective: to conclusively establish that a 95% CaF_2 flotation concentrate can be produced at roughly 75% recovery.

The scope of this preliminary evaluation programme would include:

- The identification and preparation of a representative sample;
- Grinding tests to re-confirm fluorite liberation at 80% passing 15 µm;
- Grinding tests to re-confirm rougher and scavenger recovery at 80% passing 100 µm;
- Bench flotation tests using a selection of collectors and depressants and a range of different conditioning and flotation conditions; and
- Mineralogical and chemical analyses of the flotation products.

There would be no need for optimisation at this stage. Only after the key flotation performance assumption has been verified with up-dated testwork results should the project proceed to the pre-feasibility stage.

The pre-feasibility study will require several additional components over and above the normal new fluorspar development pre-feasibility programme. In addition to the usual components, i.e. geology & mineralogy, resources, mining, processing, marketing, environment, infrastructure, services, and financial viability, the study will also need to include sections for assessing the reactivity (N rea) of the fluorspar, the bespoke modifications needed at the exclusive end users' plants, and the domestic and export markets for AlF_3 and fluoro-chemicals produced from Moina fluorspar As the justification for development of the Moina deposit will rely entirely on exclusive supply to particular end users, the pre-feasibility study would have to address the viability of all links in the chain and ensure that all components were robust. The larger than normal scale of the pre-feasibility study is a further reason to confirm in advance that a 95% CaF_2 product can be produced from wrigglite.

9.0 PROPOSED ROLE FOR DELTA MINERALS LIMITED

Delta Minerals would be pleased to design and manage the initial flotation test programme and, subject to success, would be pleased to manage the complete processing component of the pre-feasibility on behalf of Minemakers. Testwork is best completed in-country provided suitable labs and services are available. This allows local water to be used for flotation and prevents complications and delays over the movement of samples. Australia has world-class metallurgical labs which could undertake the work, however, without the experience from a local fluorspar industry, these labs lack the specialist knowledge required for fluorspar studies. Specialist experience extends to analytical services as well as metallurgical procedures. Assaying for fluorspar is widely known to be difficult, and there are several recent examples where inaccurate results caused fluorspar testwork programmes to be re-run because skilled umpire analysts in world-class labs failed to appreciate the unique procedures required for assaying fluorspar flotation concentrates. Delta Minerals would design, initially and periodically supervise, and remotely manage the testwork. As results became available, they would be interpreted and the test programme up-dated accordingly until the objectives were achieved. Delta Minerals would act as the Client's representative looking after the Client's interests throughout and always seeking the most efficient and cost-effective route to achieving the pre-established objectives. This role would be flexible and would be adjusted as necessary to accommodate the level of input felt appropriate by Minemakers at the time.

10.0 CONCLUSIONS

For easy reference, the conclusions of this brief study are summarised in bullet-point format:

- In the opinion of Delta Minerals, processing of Moina wrigglite will be difficult, but not fatally flawed. It is flawed in the sense that the production of an acidgrade concentrate which meets all international specifications is likely to be impossible, however this does not prevent HF and AlF_3 from being produced from a sub-acidgrade Moina fluorspar concentrate in HF plants specifically geared and tuned to accept this grade of fluorspar. As a supplier to compatible HF/AlF_3 plants, the Moina project has a strong potential, but as a stand-alone fluorspar producer feeding the international market, the project is fatally flawed, despite many advances in processing technology since the previous testwork in the 1970s.
- The primary concern to the consumer will be the very fine particle size of the product. It would be essential for standard HF plants to be modified with tailor-made fine particle handling and dust controls before this product could be used.
- By integrating the Moina operation as the exclusive supplier to the existing aluminium and fluoro-chemical industries in Australia, these industries would gain a long-term secure non-Chinese non-developing country source of raw material. This strategy would lead to an economic edge over their competitors and an economic benefit to Australia as a whole. Moreover the price of fluorspar is currently at a historical high while stocks are at a historical low.
- There would be no abnormal complications with the processing flowsheet, but operating costs would be unusually high due to the need for very fine grinding.
- Moina fluorspar would carry the advantages of no P_2O_5, arsenic, or lead and a low sulphur content, but would suffer the disadvantages of high Fe_3O_4 and SiO_2 contents and, most importantly, a very fine particle size.
- The option of processing the ore to metallurgical grade fluorspar is fatally flawed. Due to the intimate association of the fluorite with silicates, it would

be impossible to reach the necessary 60 effective CaF_2 units without fine grinding, flotation, and briquetting. These are high operating cost processes which would make the product uncompetitive and uneconomic. Moreover, metallurgical grade viability will not improve with the passing time due to the progressively diminishing and progressively more environmentally-sensitive end use.

- While the benefit from the other economic minerals will be significant due to their high prices, their recoveries will be limited. Cassiterite recovery by gravity separation will likely be less than 20% and the grade poor, and some of the past testwork indicates that any recovery at all may be optimistic. However cassiterite flotation was not tested and this method of separation is likely to provide the highest recovery. The recovery of the scheelite is likely to be less than 70%, and, although the recovery of the sulphides (with gold) should be higher, estimated at 70% to 80%, the grade is likely to be lower than standard. A magnetite-rich concentrate will be recovered, and there is a possibility of recovering further magnetite from the flotation tailings. However the resulting SG is unknown, putting magnetite marketability and value for heavy media uses in doubt. The particle size of the garnet would meet only the finest ANSI polishing grade specifications, and as this represents a speciality market only, the garnet will not contribute significantly to the revenue of the project.
- The inferred resource of 26.5 Mt at 18% CaF_2 would be sufficient to sustain an output of 180,000 t/y of fluorspar filtercake for at least 21 years from the Comalco area, and this life would be extended using the resources known to exist but not measured in the immediately surrounding areas.
- The geographic location, pre-existing infrastructure and facilities, and shallow deposit at Moina carry competitive advantages over many alternative sources of fluorspar from currently proposed new projects.
- Moina is outside the near-by environmentally sensitive areas and there should be no restrictions preventing development of the project, and the availability of plentiful supplies of soft fresh water is a particular benefit for fluorspar processing.

APPENDIX 2:
STANDARD TEST METHODS FOR ANALYSIS OF FLUORSPAR

Designation: E 1506 – 97 (Reapproved 2003)

Standard Test Methods for Analysis of Acid-Grade Calcium Fluoride (Fluorspar)[1]

This standard is issued under the fixed designation E 1506; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 These test methods cover the chemical analyses of acid-grade calcium fluoride (fluorspar). These test methods appear in the following sections:

	Sections
Volatiles as Moisture	6-13
Silica	14-22
Assay as Calcium Fluoride (CaF_2)	23-32
Soluble Chloride as NaC1	33-50
Calcium Carbonate	51-59
Phosphorus	60-69
Arsenic	70-78
Mixed Oxides (R_2O_3)	79-87
Sulfide Sulfur	88-96

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

1.4 Review the current Material Safety Data Sheet (MSDS) for each chemical used in this standard for detailed information concerning toxicity, first-aid procedures, handling, and safety precautions.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals[3]

E 300 Practice for Sampling Industrial Chemicals[4]

3. Significance and Use

3.1 Calcium fluoride is available in nature in various forms and purities. A major use for it is in the manufacture of hydrofluoric acid. The test methods listed in 1.1 provide procedures for analyzing calcium fluoride to determine whether it is suitable for this use.

4. Reagents

4.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[5] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

4.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type II or Type III reagent water conforming to Specification D 1193.

5. Sampling

5.1 Sampling of calcium fluoride is not within the scope of these test methods. See the appropriate sections of Practice E 300 for sampling procedures.

VOLATILES AS MOISTURE

6. Scope

6.1 This test method covers the determination of volatiles as percent moisture.

7. Summary of Test Method

7.1 The sample is dried in an air oven at 105 to 110°C, and the weight loss is calculated as percent moisture.

8. Apparatus

8.1 *Top-Loading Balance*, capable of weighing 1000 g to the nearest 0.01 g.

8.2 *Sample Pan*, stainless steel or borosilicate glass, 152 by 152 by 51 mm (6 by 6 by 2 in.) deep.

8.3 *Cooling Rack*, wood or metal, able to allow circulation of air around the entire sample pan (for example, a "baker's rack").

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[1] These test methods are under the jurisdiction of ASTM Committee E15 on Industrial and Specialty Chemicalsand are the direct responsibility of Subcommittee E15.02 on Product Standards.

Current edition approved Apr. 10, 2003. Published May 2003. Originally approved in 1994. Last previous edition approved in 1997 as E 1506 – 97.

[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 15.05.

[4] Discontinued. See 2000 *Annual Book of ASTM Standards*, Vol 15.05.

[5] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

TABLE 1 Volatiles as Moisture Checking Limits for Duplicates

Volatiles Level, %	Standard Deviation	Degrees of Freedom	95 % Limit, % Absolute
6	0.0257	18	0.072
9	0.0822	18	0.230

8.4 *Forced Air Oven*, capable of maintaining temperatures of 105 to 110°C.

9. Hazards

9.1 See 1.3 and 1.4.

10. Procedure

10.1 Tare a clean, dry sample pan to the nearest 0.01 g.

10.2 Add approximately 1000 g of representative sample to the pan and spread evenly. Wipe all external surfaces of the pan free of sample. Weigh again to the nearest 0.01 g.

10.3 Place the pan containing the sample in an air oven at 105 to 110°C for a minimum of 12 h.

10.4 Remove the pan from the oven and place on a cooling rack for 1 h.

10.5 Weigh the cooled pan to the nearest 0.01 g.

10.6 Return the pan to the cooling rack and cool for an additional 30 min. Then reweigh the pan to the nearest 0.01 g.

10.7 Repeat 11.6 until consecutive weights agree within 0.05 g.

10.8 Once a consistent weight has been obtained, dump the sample on a flat, dry surface and spread it with a spatula. If the fluorspar is dry, it will appear dusty, powdery, and flour-like in consistency. If the fluorspar does not appear as such, repeat the analysis using fresh sample.

11. Calculation

11.1 Calculate percent volatiles as moisture as follows:

$$\text{volatiles as moisture, weight \%} = \frac{(B - C) \times 100}{(B - A)} \qquad (1)$$

where:

A = weight of empty pan, g (10.1),
B = weight of pan plus sample before drying, g (10.2), and
C = weight of pan plus sample after drying to consistent weight, g (10.7).

12. Report

12.1 Report the percent volatiles as moisture to the nearest 0.01 %.

13. Precision and Bias

13.1 *Precision*—The following criteria should be used for judging the acceptability of results (see Note 1):

13.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be the value shown in Table 1 at the indicated degrees of freedom. The 95 % limit for the difference between two such runs is the value shown in Table 1.

13.1.2 *Laboratory Precision (Within-Laboratory, Between-Days)*—The standard deviation of results (each the average of duplicates) obtained by the same analyst on different days has been estimated to be the value shown in Table 2 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is the value shown in Table 2.

TABLE 2 Volatiles as Moisture

Volatiles Level,%	Repeatability			Reproducibility		
	Standard Deviation	Degrees of Freedom	95 % Limit, % Absolute	Standard Deviation	Degrees of Freedom	95 % Limit,% Absolute
6	0.0238	9	0.067	0.0807	8	0.226
9	0.0666	9	0.186	0.0865	8	0.242

13.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates) obtained by analysts in different laboratories has been estimated to be the value shown in Table 2 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is the value shown in Table 2.

NOTE 1—These precision estimates are based on an interlaboratory study performed in 1992 in which samples of fluorspar from two lots, one containing about 6 % volatiles as moisture and the other about 9 % volatiles as moisture, were each analyzed in duplicate by one analyst on each of two days in each of ten laboratories for a total of 120 determinations.[6] Practice E 180 was used in developing these precision estimates.

13.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

SILICA

14. Scope

14.1 This test method covers the determination of percent silica.

15. Summary of Test Method

15.1 The sample is treated with 10 % acetic acid to remove carbonates and soluble salts, the residue is ignited in a 650°C muffle furnace, treated with 48 % hydrofluoric acid (HF), and then heated again at 650°C. The weight loss after the HF treatment is calculated as percent silica.

16. Apparatus

16.1 *Analytical Balance*, capable of weighing to the nearest 0.1 mg.

16.2 *Beaker*, 150-mL glass, unscratched, and watchglass cover.

16.3 *Graduated Cylinder*, 25-mL glass.

16.4 *Graduated Cylinder*, 10-mL polypropylene.

16.5 *Platinum Crucible*, 30-mL capacity with lid.

16.6 *Platinum Wire*, 4 cm by 2 mm.

16.7 *Stirring Rod*, borosilicate glass, unscratched.

16.8 *Muffle Furnace*, capable of maintaining a temperature of 650 ± 10°C or higher.

16.9 *Desiccator*, with desiccant.

16.10 *Steam Bath.*

16.11 *Glass Filter Funnel.*

16.12 *Bunsen Burner*, ringstand, ring, and heating mesh.

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[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: E15-1027.

16.13 *Disposable Pipets.*

16.14 *Mortar and Pestle*, 102-mm (4-in.) diameter, agate.

16.15 *Tongs*, platinum-tipped.

17. Reagents

17.1 *Acetic Acid Solution* (100 mL/L)—Dilute 10 mL of glacial acetic acid to 100 mL with water; mix well.

17.2 *Hydrofluoric Acid* (HF), 48 %.

17.3 *Ashless Cellulose Filter Aid*, Whatman accelerator powder,[7] or equivalent.

17.4 *Filter Paper*, 9-cm diameter, low-ash, acid-washed, medium-porosity, able to retain 8-μm particles.

17.5 *Filter Paper*, 9-cm diameter, low-ash, acid-washed, fine-porosity, able to retain 2.5-μm particles.

17.6 *Ethanol*, pure or denatured.

17.7 *Filter Pulp Slurry* (40 g/L)—Slurry 10 g of cellulose filter aid with 250 mL of water.

18. Hazards

18.1 See 1.3 and 1.4.

19. Procedure

19.1 Transfer 8 to 10 g of sample (previously dried to constant weight at 105 to 110°C) into a mortar. Grind with a pestle until the particle size is 100 to 500 mesh.

19.2 Weigh 1.0 g of the ground sample to the nearest 0.0001 g, and transfer it to a 150-mL beaker.

19.3 Wet the sample with 1 mL of ethanol, then add 15 mL of 10 % acetic acid to the beaker.

19.4 Add a glass stirring rod to the beaker, cover with a watchglass, and place on a steam bath.

19.5 Heat for 30 ± 1 min, stirring every 5 min.

19.6 Remove from the steam bath, add 5 mL of filter pulp slurry to the beaker, cover, and allow to sit for approximately 12 h.

19.7 Gravity filter the solution through medium-porosity filter paper.

19.8 Rinse the beaker several times with minimal portions of hot water (total wash water approximately 35 mL), filtering each wash through the same filter paper. Save the filtrate for the determination of Mixed Oxides (Section 79).

19.9 Wipe the beaker clean with one fourth of a fine-porosity filter paper, and transfer the wipe paper and the filter paper with the residue into a 30-mL platinum crucible.

19.10 Place a platinum wire across the top of the platinum crucible. Rest the crucible lid on the wire and place the crucible into a cool muffle furnace.

19.11 Heat the furnace slowly (1-h cycle) to 650 ± 10°C. Once the temperature has reached 650°C, check the crucible every 10 min until the paper is entirely burned off.

19.12 Cool the crucible to room temperature in a desiccator, then weigh the crucible, cover, and residue to 0.0001 g.

19.13 Using a 10-mL polypropylene graduate cylinder, carefully pour 3 mL of 48 % HF into the crucible.

19.14 Gently heat the crucible over a Bunsen burner in a hood until dry (see Note 2).

NOTE 2—The solution must be heated below boiling. Excess heat will cause erratic results. If unable to control heating using a bunsen burner, heat the solution on a hot plate at 60°C or below. Evaporation of the 6 mL of HF used in this procedure should take approximately 2 h.

19.15 Cool the crucible, then repeat 19.13 and 19.14.

19.16 Cover the crucible with a platinum lid; then carefully place it into a muffle furnace maintained at 650 ± 10°C.

19.17 Heat the crucible for 5 min; then place it into a desiccator to cool.

19.18 Weigh the crucible, cover, and residue to 0.0001 g.

20. Calculation

20.1 Calculate percent silica as follows:

$$\text{silica, weight \%} = \frac{(B - C) \times 100}{A} \qquad (2)$$

where:

A = weight of sample, g (19.2),

B = weight of crucible, cover, and residue before HF treatment, g (19.12), and

C = weight of crucible, cover, and residue after HF treatment, g (19.18).

21. Report

21.1 Report the percent silica to the nearest 0.01 %.

22. Precision and Bias

22.1 *Precision*—The following criteria should be used for judging the acceptability of results (see Note 3):

22.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.0319 % absolute at 50 df. The 95 % limit for the difference between two such runs is 0.09 % absolute.

22.1.2 *Laboratory Precision (Within-Laboratory, Between-Days)*—The standard deviation of results (each the average of duplicates) obtained by the same analyst on different days has been estimated to be 0.0362 % absolute at 25 df. The 95 % limit for the difference between two such averages is 0.10 % absolute.

22.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates) obtained by analysts in different laboratories has been estimated to be 0.0529 % absolute at 11 df. The 95 % limit for the difference between two such averages is 0.15 % absolute.

NOTE 3—These precision estimates are based on an interlaboratory study performed in 1992 in which samples of fluorspar from two lots, one containing about 0.5 % silica and the other about 1 % silica, were each analyzed in duplicate on each of two days by one analyst in each of 14 laboratories for a total of 112 determinations.[6] Practice E 180 was used in developing these precision estimates.

22.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

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[7] Available from Whatman LabSales, P.O. Box 1359, Hillsboro, OR, 97123-9981.

ASSAY AS CALCIUM FLUORIDE (CaF_2)

23. Scope

23.1 This test method covers the determination of assay as percent calcium fluoride (CaF_2).

24. Summary of Test Method

24.1 The residue remaining after the determination of silica (see 19.18) is treated with H_2SO_4, dried, then dissolved in HCl. Ammonium oxalate is added to the HCl solution to precipitate calcium oxalate, then the precipitate is dried and weighed. Percent CaF_2 is calculated from the weight of the calcium oxalate collected.

25. Interferences

25.1 Iron causes a positive interference. If iron is suspected to be present, its effect can be minimized by adding 1 mL of concentrated HNO_3 to the solution described in 29.8 before boiling.

25.2 Strontium precipitates, as the oxalate, along with calcium oxalate to produce erroneously high results.

25.3 A small amount of CaF_2 is lost in the acetic acid treatment used in 19.3, resulting in an erroneously low result. To correct for this loss, the term 0.15 is included in the calculation in 30.1.

26. Apparatus

26.1 *Analytical Balance*, capable of weighing to the nearest 0.1 mg.

26.2 *Beakers*, borosilicate glass, 800-mL, 400-mL, and watchglass covers.

26.3 *Graduated Cylinders*, borosilicate glass, 10-mL, 25-mL.

26.4 *Platinum Crucible*, 30-mL capacity with lid.

26.5 *Platinum Wire*, 4 cm by 2 mm.

26.6 *Stirring Rod*, borosilicate glass.

26.7 *Muffle Furnace*, capable of maintaining a temperature of 1200 ± 10°C or higher.

26.8 *Desiccator*, with desiccant.

26.9 *Funnel*, borosilicate glass.

26.10 *Bunsen Burner*.

26.11 *Ringstand*, equipped with ring and heating gauze.

26.12 *Tongs*, platinum- or nickel-tipped.

27. Reagents

27.1 *Sulfuric Acid* (sp gr 1.84)—Concentrated sulfuric acid (H_2SO_4).

27.2 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl).

27.3 *Hydrochloric Acid Solution* (1 + 1)—Wearing goggles, carefully add 250 mL of concentrated HCl (sp gr 1.19) to 250 mL of water. Mix well.

27.4 *Ammonium Chloride* (NH_4Cl).

27.5 *Ammonium Hydroxide* (sp gr 0.90)—Concentrated ammonium hydroxide (NH_4OH).

27.6 *Ammonium Oxalate Solution (Saturated)*—Add 30 g of ammonium oxalate to a 1-L polyethylene bottle. Add 1000 mL of hot water to the bottle and mix well. Allow the solution to cool. Add additional ammonium oxalate if necessary to keep crystals present at the bottom of the bottle at all times.

27.7 *Ammonium Oxalate Solution* (1 g/L)—Add 0.1 g of ammonium oxalate to 100 mL of water and mix well.

27.8 *Filter Paper*, 9-cm diameter, low-ash, acid-washed, medium-porosity, able to retain 8-μm particles.

27.9 *Filter Pulp Slurry* (40 g/L)—Slurry 10 g of cellulose filter aid with 250 mL of water.

27.10 *pH Paper*—Litmus.

28. Hazards

28.1 See 1.3 and 1.4.

29. Procedure

29.1 Add 5 mL of concentrated sulfuric acid to the residue remaining in the crucible from 19.18.

29.2 Partially cover the crucible and gently heat over a bunsen burner in a hood until all H_2SO_4 is driven off (see Note 4).

NOTE 4—Do not heat directly with the flame.

29.3 Repeat 29.1 and 29.2 using 3 mL of concentrated sulfuric acid.

29.4 Cool the crucible and transfer the crucible, cover, and residue into a 400-mL beaker.

29.5 Add 10 mL of concentrated hydrochloric acid, 5 g of ammonium chloride, and 200 mL of hot water to the beaker; mix well.

29.6 Warm the solution to between 70 and 80°C on a hot plate in a hood; keep at this temperature for 2 h.

29.7 Remove the crucible and lid from the solution using platinum or nickel-tipped tongs. Rinse each with warm water, collecting the washings in the beaker. Scrape any remaining residue from the crucible into the solution with a rubber policeman.

29.8 Cover with a watchglass, then boil the solution for 10 min to dissolve any solid matter (see Note 5 and 25.1).

NOTE 5—If insolubles are still present after the 10-min boil, filter the solution through medium-porosity filter paper, then return the residue and paper to the crucible. Place platinum wire across the top of the crucible, rest the lid on the wire, and place the crucible into a cool muffle furnace. Heat the furnace slowly to 650°C (±10°C, 1-h cycle). At 650°C, check the crucible every 10 min until the paper burns off. Repeat 29.1 to 29.8 using 1 mL of concentrated sulfuric acid. Combine the filtrates in one beaker, then continue with 29.9.

29.9 Allow the solution to cool, then add ammonium hydroxide dropwise while mixing, until the solution tests basic (blue) to Litmus paper.

29.10 Mix well, cover, and then boil for 1 min.

29.11 Allow the solution to cool slightly. If necessary, add ammonium hydroxide dropwise while mixing until the solution tests basic (blue) to Litmus paper.

29.12 Gravity filter this solution through medium-porosity filter paper, into an 800-mL beaker.

29.13 Wash the filter paper and residue several times with hot water, collecting the filtrates in the 800-mL beaker (see 29.12).

29.14 Wash the filter paper and residue with 20 mL of hot 1 + 1 HCl solution, then four 20-mL portions of hot distilled water, collecting the filtrates in the 400-mL beaker.

29.15 Adjust the pH of the solution in the 400-mL beaker with ammonium hydroxide until it tests basic (blue) to Litmus paper.

29.16 Boil this solution for 1 min, then allow to cool slightly just below boiling.

29.17 Filter through the original filter paper. Wash with hot water and collect the filtrate in the 800-mL beaker. Save the filter cake for the determination of Mixed Oxides (Section 79). Bring the filtrate to a boil. Add 100 mL of saturated ammonium oxalate solution, then add 5 mL of filter pulp slurry and stir to mix.

29.18 Boil the solution for 30 s, then allow it to cool until precipitate settles. The sample can sit overnight before filtering, if necessary or convenient.

29.19 Gravity filter the solution through medium-porosity filter paper.

29.20 Rinse the beaker with 10 to 15 mL of cold 0.1 % ammonium oxalate solution. Transfer the washings into the filter, using them to wash the precipitate.

29.21 Repeat 29.20 two more times.

29.22 Wash the residue with three 10 to 15-mL portions of 0.1 % ammonium oxalate solution.

29.23 Wash the residue with three 10 to 15-mL portions of cold water.

29.24 Weigh a 30-mL platinum crucible and cover to 0.0001 g (Weight *B*).

29.25 Transfer the filter paper and residue into the platinum crucible.

29.26 Place a platinum wire across the top of the platinum crucible, rest the lid on the wire, and place the crucible into a cool muffle furnace.

29.27 Heat the furnace slowly to 1200°C. Check to see if all paper is burned off.

29.28 Keep crucible at 1200°C for 20 min.

29.29 Remove crucible and place in a desiccator containing fresh desiccant; allow to cool to room temperature.

29.30 Immediately weigh the crucible, cover, and residue to 0.0001 g (Weight *C*).

30. Calculation

30.1 Calculate assay as percent CaF_2 as follows:

$$\text{assay as } CaF_2\text{, weight \%} = \frac{(C - B) \times 1.3923 \times 100}{A} + 0.15 \quad (3)$$

where:

A = weight of fluorspar sample, g, (see 19.2),
B = weight of crucible and cover, g, (see 29.24),
C = weight of crucible, cover, and residue, g (see 29.30),
1.3923 = conversion factor for CaO (molecular weight (MW) = 56.08) to CaF_2(MW = 78.08), and
0.15 = correction for amount of calcium fluoride lost in the acetic acid treatment, considered to be 0.0015 g CaF_2/g sample.

31. Report

31.1 Report the percent calcium fluoride to the nearest 0.01 %.

32. Precision and Bias

32.1 *Precision*—The following criteria should be used for judging the acceptability of results (see Note 6):

32.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.1778 % absolute at 30 df. The 95 % limit for the difference between two such runs is 0.50 % absolute.

32.1.2 *Laboratory Precision (Within-Laboratory, Between-Days)*—The standard deviation of results (each the average of duplicates) obtained by the same analyst on different days has been estimated to be 0.1169 % absolute at 15 df. The 95 % limit for the difference between two such averages is 0.33 % absolute.

32.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates) obtained by analysts in different laboratories has been estimated to be 0.3559 % absolute at 6 df. The 95 % limit for the difference between two such averages is 1.00 % absolute.

NOTE 6—These precision estimates are based on an interlaboratory study performed in 1992 on two samples (one a commercial sample, the other a reference material) each containing approximately 98 % calcium fluoride. One analyst in each of eight laboratories performed duplicate determination of a sample of NIST Standard Reference Material 79a on each of two separate days for a total of 32 determinations. The same protocol was used on a sample of commercial material except that seven laboratories participated for a total of 28 determinations.[6] Practice E 180 was used in developing precision estimates.

32.2 *Bias*—An average of 97.71 % calcium fluoride was obtained on NIST Standard Reference Material 79a which has a certified value of 97.39 %. This certified value, with a standard deviation of 0.06 % absolute for a single determination, was obtained using the U.S. Customs Laboratory Method (volumetric permanganate) as given in the certificate.

SOLUBLE CHLORIDE AS NaCl

33. Volumetric Procedure, Scope

33.1 This test method covers the volumetric determination of trace quantities of soluble chloride as percent NaCl.

34. Summary of Test Method

34.1 Soluble chloride is extracted from fluorspar with hot water; the extract is filtered, then titrated to a colorimetric end point with standardized silver nitrate solution.

35. Apparatus

35.1 *Analytical Balance*, capable of weighing to the nearest 0.1 mg.

35.2 *Pipets*, 1-mL, 10-mL glass.

35.3 *Graduated Cylinder*, 100-mL glass.

35.4 *Beakers*, 150-mL, 250-mL.

35.5 *Burets*, 10-mL, 25-mL glass.

35.6 *Volumetric Flask*, 1-L glass.

36. Reagents

36.1 *Potassium Chromate Indicator Solution* (50 g/L)—Dissolve 50 g K_2CrO_4 in 500 mL of water. Add silver nitrate solution (see 36.3) until a definite red precipitate is formed. Allow to stand 12 h, filter through fine-porosity filter paper and dilute the filtrate to 1 L with water.

36.2 *Sodium Chloride Standard Solution* (0.0141 *N*)—Dissolve 0.8241 g of NaCl (previously dried to constant weight at 105 to 110°C) in water and dilute to 1 L; mix well.

36.3 *Silver Nitrate Standard Titrant* (0.0141 *N*)—Dissolve 2.395 g of $AgNO_3$(previously dried to constant weight at 105 to 110°C) in water and dilute to 1 L; mix well.

36.3.1 Pipet 10.0 mL of 0.0141 *N* NaCl (see 36.2) into a 150-mL beaker, add 40 mL of water and 1 mL of K_2CrO_4 indicator solution. Using a 25-mL buret, titrate this solution with the 0.0141 *N* $AgNO_3$ to a faint brown end point (see Note 7). Similarly determine a blank using all of the above reagents, but no NaCl. The titer of the $AgNO_3$ in µg Cl/mL, *A*, is as follows:

$$A = \frac{(500 \times 10)}{B} \tag{4}$$

where:

500 = Cl in 0.0141 *N* NaCl, µg/mL, and

B = $AgNO_3$ required for titration of the solution, net mL.

Store standardized solution in a brown glass bottle.

36.4 *Filter Paper*, 12.5-cm diameter, fine-porosity.

36.5 *Denatured Alcohol.*

37. Hazards

37.1 See 1.3 and 1.4.

38. Procedure

38.1 Weigh 25 g of sample (previously dried to constant weight at 105 to 110°C) to the nearest 1 g into a 150-mL beaker; wet the sample with 10 mL of denatured alcohol.

38.2 Add 100 mL of hot distilled water to the beaker. Using a magnetic stirrer, stir the mixture for 1 h; allow the mixture to cool and the fluorspar to settle.

38.3 After a minimum of 2-h settling time, gravity-filter the solution through a 12.5-cm diameter fine-porosity filter paper, collecting the filtrate in a 250-mL beaker.

38.4 Pipet 1 mL of potassium chromate indicator solution into the beaker.

38.5 Using a 10-mL buret, titrate with 0.0141 *N* $AgNO_3$ dropwise to a faint brown end point; mL = *A* (see Note 7).

NOTE 7—To aid in the determination of the end point, place a 250-mL beaker with the same volume of water and indicator next to the sample, as a comparator. The first brownish color that appears in the sample is the end point.

38.6 Similarly, determine a blank using all of the above reagents, but no sample; mL = *B*.

39. Calculation

39.1 Calculate percent soluble chloride as NaCl as follows:

$$\text{Soluble chloride as NaCl, weight \%} = \frac{(A - B) \times C \times 1.6485}{D \times 10^4} \tag{5}$$

where:

A = 0.0141 *N* $AgNO_3$ used for sample, mL,

B = 0.0141 *N* $AgNO_3$ used for blank, mL,

C = Cl/mL of titrant, µg,

D = weight of sample, g (see 38.1), and

1.6485 = conversion Cl (MW = 35.45) to NaCl (MW = 58.45); and 58.56/35.45 = 1.6485.

40. Report

40.1 Report the soluble chloride as NaCl to the nearest 0.01 %.

41. Precision and Bias

41.1 *Precision*—The following criteria should be used for judging the acceptability of results (see Note 8):

41.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.00068% absolute with 32 df. The 95 % limit for the difference between two such determinations is 0.002 % absolute.

41.1.2 *Laboratory Precision (Within-Laboratory, Between-Days)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.00035 % absolute with 16 df. The 95 % limit for the difference between two such averages is 0.001 % absolute.

41.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 0.0012 % absolute with 7 df. The 95 % limit for the difference between two such averages is 0.004 % absolute.

41.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

NOTE 8—These precision estimates are based on an interlaboratory study performed in 1993 on two samples of acid-grade fluorspar containing approximately 0.001 and 0.002 % sodium chloride. One analyst in each of eight laboratories performed duplicate determinations on each of two days for a total of 64 determinations.[6] Practice E 180 was used in developing the precision data.

42. Ion Chromatography Procedure, Scope

42.1 This test method covers the ion-chromatography determination of trace quantities of soluble chloride as µg/g (ppm) NaCl.

43. Summary of Test Methods

43.1 Soluble chloride is extracted from fluorspar with hot water, the extract made to volume, filtered, and then the chloride concentration is determined by ion chromatography.

44. Apparatus

44.1 *Balance*, capable of weighing to the nearest 0.1 g.

44.2 *Volumetric Flask*, 250-mL.

44.3 *Filter Medium*, chloride-free, 0.45-µm pore size, or less. (Gelman IC Acrodiscs fitted to a syringe work well.)

44.4 *Ion Chromatographic System*, able to produce baseline separation of fluoride, chloride, nitrate, phosphate, and sulfate.[8]

45. Reagents

45.1 *Chloride Standard*[9]—Dilute the standard with deionized water to a chloride concentration within the linear range of the detector and near the chloride level in the sample extract.

45.2 *Deionized Water*, chloride-free.

46. Hazards

46.1 See 1.3 and 1.4.

47. Procedure

47.1 Weigh 25 g of sample (previously dried to constant weight at 105 to 110°C) to the nearest 0.1 g into a 250-mL volumetric flask. Add 200 mL of hot (near boiling) deionized water to the flask. Using a magnetic stirrer, stir the sample for 1 h.

47.2 Cool the sample to room temperature under running water, make to volume with deionized water, then mix well.

47.3 Allow most of the fluorspar to settle (15 to 20 min), then filter a portion of the solution through a chloride-free, fine-porosity (0.45 µm, or less) filtered medium.

47.4 Chromatograph a portion of the filtrate, then compare the area of the resultant chloride peak to that of a chloride standard similarly chromatographed.

NOTE 9—If the chloride level of the filtrate is such that the resultant peak is outside the linear range of the detector, dilute the extract appropriately with deionized water and rechromatographed.

48. Calculation

48.1 Calculate the soluble chloride concentration as µg/g (ppm) NaCl as follow:

$$\text{Soluble chloride as NaCl, } \mu g/g \text{ (ppm)} = \frac{A \times B \times 1.6485 \times 9.60 \times C}{D} \quad (6)$$

where:

A = area of sample peak,

B = µg/g chloride in the standard,

1.6485 = conversion Cl (MW 35.45) to NaCl (MW 58.45) = 58.45/35.45 = 1.6485,

9.60 = 250/25 × 0.96,

250/25 = dilution factor,

0.96 = adjustment to dilution factor required since 25 g of sample displaces approximately 10 mL water,

C = any additional dilution factor needed to keep the Cl peak within the linear range of the detector, and

D = area of standard peak.

49. Report

49.1 Report soluble chloride as NaCl to the nearest 0.1 µg/g (ppm).

50. Precision and Bias

50.1 *Precision*—Use the following criteria for judging the acceptability of results (see Note 10):

50.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 1.26 µg/g with 18 df. The 95 % limit for the difference between two such determinations is 3.53 µg/g.

50.1.2 *Laboratory Precision (Within-Laboratory, Between-Days)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 1.08 µg/g with 9 df. The 95 % limit for the difference between two such averages is 3.02 µg/g.

50.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 2.26 µg/g with 8 df. The 95 % limit for the difference between two such averages is 6.32 µg/g.

50.1.4 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

NOTE 10—These precision estimates are based on an interlaboratory study performed in 1995 on one sample of acid-grade fluorspar containing approximately 15 µg/g of sodium chloride. One analyst in each of ten laboratories performed duplicate determinations on each of two days for a total of 40 determinations.[6] Practice E 180 was used in developing the precision data.

CALCIUM CARBONATE

51. Scope

51.1 This test method covers the determination of calcium carbonate in the range from 0 to 2 %.

52. Summary of Test Method

52.1 Calcium carbonate is extracted from fluorspar with dilute acetic acid; the extract is made alkaline with potassium hydroxide, and then calcium is titrated with disodium ethylenediaminetetraacetate (EDTA) solution using hydroxynaphthol blue as an indicator and calculated as calcium carbonate.

53. Apparatus

53.1 *Analytical Balance*, capable of weighing to the nearest 0.1 mg.

53.2 *Beakers*, 600, 400, 250, and 150-mL glass, unscratched, and watchglass covers.

53.3 *Graduated Cylinders*, 100, 25, and 10-mL.

53.4 *Stirring Rod*, borosilicate glass, unscratched.

53.5 *Steam Bath*.

53.6 *Glass Filter Funnel*.

53.7 *Mortar and Pestle*, 102-mm (4-in.) diameter, agate.

53.8 *Buret*, Class A, 50-mL, 0.1-mL division, polytetrafluoroethylene stopcock.

53.9 *Volumetric Flask*, 1-L.

53.10 *Hot Plate*, stirrer.

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[8] A system known to produce adequate separation includes a DIONEX Model 20101 Ion Chromatograph equipped with a CDM-2 detector set at 10 µS; a DIONEX AS4A anion column, AG4A guard column and ASRS suppresser column; an eluant consisting of 1.7 mM $NaHCO_3$ in 1.8 mM Na_2CO_3; isocratic elution at 2.0 mL/min; a 50-µL sample injection.

[9] Use DIONEX Five Anion Standard Part No. 037157, or similar.

53.11 *Pipet*, 50-mL.

54. Reagents

54.1 *Acetic Acid Solution* (100 mL/L)—See 17.1.

54.2 *Ashless Cellulose Filter Aid*—Whatman accelerator powder,[7] or equivalent.

54.3 *Filter Paper*, 9-cm—See 17.4.

54.4 *Ethanol*—Pure or denatured.

54.5 *Filter Pulp Slurry* (40 g/L)—See 17.7.

54.6 *Litmus Paper.*

54.7 *Hydroxynaphthol Blue Indicator*—Fisher Scientific H346-100,[10] calcium indicator, or equivalent.

54.8 *Potassium Hydroxide* (30 % weight/volume)—Dissolve 300 g of potassium hydroxide (KOH) in water and dilute to 1 L; mix well. Store in a plastic bottle.

54.9 *Triethanolamine Solution* (1 + 1)—Mix 50 mL of triethanolamine ($NC_6H_{15}O_3$) with 50 mL of water; mix well.

54.10 *Calcium Carbonate* ($CaCO_3$)—High purity, minimum 99.95 %.

54.11 *Hydrochloric Acid* (1 + 10)—Mix 1 volume of concentrated hydrochloric acid (HCl) with 10 volumes of water.

54.12 *Disodium Ethylenediaminetetraacetate (EDTA) Standard Solution* (0.025 M)—Dissolve 9.3062 g of disodium ethylenediaminetetraacetate dihydrate ($C_{10}H_{14}N_2Na_2O_8{\cdot}2H_2O$)[10] in water. Transfer the solution to a 1-L volumetric flask; dilute to volume with water; and mix well. Standardize as follows.

54.12.1 Dry 3 g of $CaCO_3$ in a 110°C oven for 1 h. Remove from oven and allow to cool in a desiccator. Weigh 2.4970 g of the dried $CaCO_3$ into a 600-mL beaker, cautiously add 75 mL of 1 + 10 HCl to the beaker, cover, and warm gently to dissolve the $CaCO_3$. Cool the solution and transfer into a 1-L volumetric flask, dilute to volume with water, and mix well (solution concentration: 1 mL = 1.0000 mg of Ca).

54.12.2 Pipet 50 mL of the solution prepared in 54.12.1 into a 400-mL beaker, add 5 mL of 1 + 1 triethanolamine to the beaker, and dilute to 200 mL with water. Dropwise, add 30 % KOH until the solution tests neutral with litmus paper. Add an additional 10 mL of 30 % KOH to the solution and mix well.

54.12.3 Add 0.5 g hydroxynaphthol blue indicator and titrate immediately with 0.025 *M* EDTA solution to a blue end point. Record *A*, the millilitres of EDTA required for the titration.

$$\text{calcium oxide equivalent of EDTA in g CaO/mL EDTA} = 50.0/A \times 1.3992 \times 0.001 = F \quad (7)$$

where:

50.0 = mL of $CaCO_3$ solution used in titration,
A = mL of EDTA solution used for titration,
1.3992 = conversion factor for calcium to calcium oxide, MW CaO = 56.08/MW Ca = 40.08, and
0.001 = conversion of mg to g.

54.12.4 Standardize the EDTA solution in triplicate using the steps described in 54.12.2 and 54.12.3, and average the three results to the nearest 0.000001 g/mL.

55. Hazards

55.1 See 1.3 and 1.4.

56. Procedure

56.1 Transfer 8 to 10 g of sample (previously dried to constant weight at 105 to 110°C) into a mortar. Grind with a pestle until the particle size is 100 to 500 mesh.

56.2 Weigh 1.0 g of the ground sample to the nearest 0.0001 g, and transfer it to a 150-mL beaker.

56.3 Wet the sample with 1 mL of ethanol, then add 15 mL of acetic acid (100 mL/L) to the beaker.

56.4 Add a glass stirring rod to the beaker, cover with a watchglass, and place on a steam bath.

56.5 Heat for 30 ± 1 min, stirring every 5 min.

56.6 Remove from the steam bath, add 5 mL of filter pulp slurry to the beaker, cover, and allow to sit for approximately 12 h.

56.7 Gravity-filter the solution through medium porosity filter paper.

56.8 Rinse the beaker several times with minimal portions of hot water (total wash water approximately 35 mL), filtering each wash through the same filter paper.

56.9 Add 5 mL of triethanolamine solution to the filtrate in a 250-mL beaker.

56.10 Dropwise, add 30 % KOH to the solution until it tests neutral with litmus paper.

56.11 Add 10 mL additional 30 % KOH; mix well.

56.12 Add 0.5 g of hydroxynaphthol blue indicator to the solution; mix well.

56.13 Titrate the solution with standardized 0.025 *M* EDTA solution to a blue end point. Record *C*, the millilitres of EDTA required for the titration.

57. Calculation

$$\%\,CaCO_3 = \frac{[(C \times F) - 0.0010] \times 1.7848 \times 100}{B} \quad (8)$$

where:

C = mL of 0.025 *M* EDTA solution used in titration (56.13),
B = sample weight (56.2),
F = factor representing g CaO/mL EDTA (54.12.4),
0.0010 = correction for calcium fluoride dissolved in the acetic acid treatment, estimated to be 0.0010 g/g of sample, and
1.7848 = conversion factor for CaO (MW = 56.08) to $CaCO_3$(MW = 100.09) (that is, 100.09/56.08 = 1.7848).

58. Report

58.1 Report the percent calcium carbonate to the nearest 0.01 %.

59. Precision and Bias

59.1 *Precision*—The following criteria should be used for judging the acceptability of results (see Note 11):

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[10] Correct American Chemical Society name is (ethylenedinitrilo) tetraacetic acid disodium salt dihydrate.

59.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.0148 % absolute at 38 df. The 95 % limit for the difference between two such determinations is 0.04 % absolute.

59.1.2 *Laboratory Precision (Within-Laboratory, Between-Days)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.0156 % absolute at 19 df. The 95 % limit for the difference between two such averages is 0.04 % absolute.

59.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 0.0910 % absolute at 8 df. The 95 % limit for the difference between two such averages is 0.25 % absolute.

59.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

NOTE 11—These precision estimates are based on an interlaboratory study performed in 1994 on two samples of acid-grade fluorspar containing approximately 0.55 and 0.79 % calcium carbonate. One analyst in each of ten laboratories performed duplicate determinations on each of two days for a total of 80 determinations.[6] Practice E 180 was used in developing the precision data.

PHOSPHORUS

60. Scope

60.1 This test method covers the determination of total phosphorus.

61. Summary of Test Method

61.1 The sample is dissolved in nitric acid, fumed with perchloric acid, then reacted with ammonium molybdate to form heteropoly phosphomolybdate. The phosphomolybdate is reduced with hydrazine sulfate to form the molybdenum blue complex, which is measured at 650 nm or 825 nm, depending on the concentration of analyte. Hydrobromic acid is added to eliminate interference by arsenic.

62. Apparatus

62.1 *Spectrometer*, capable of measurements at 650 nm and 825 nm.

62.2 *Analytical Balance*, capable of weighing to the nearest 0.1 mg.

62.3 *Beakers*, 400-mL.

62.4 *Graduated cylinders*, 10-mL, 25-mL, 50-mL, 100-mL.

62.5 *Bunsen burner*, hot plate, hot water bath.

62.6 *Funnel*, No. 40 Whatman filter paper, 11-cm.

62.7 *Volumetric flasks*, 100-mL, 500-mL, 1000-mL, borosilicate glass, volumetric.

62.8 *Pipets*, 1-mL, 10-mL, 20-mL, 50-mL.

62.9 *Erlenmeyer flask*, 250-mL.

63. Reagents

63.1 *Ammonium Molybdate Solution (20 g/L)*—Add 300 mL of H_2SO_4 to 500 mL of water and cool. Add 20 g of ammonium heptamolybdate ($(NH_4)_6Mo_7O_{27}\cdot 4H_2O$), dilute to 1 L, and mix.

63.2 *Hydrazine Sulfate Solution (1.5 g/L)*—Prepare fresh daily. Dissolve 1.5 g of hydrazine sulfate ($(NH_2)_2\cdot H_2SO_4$) in water, dilute to 1 L, and mix.

63.3 *Ammonium Molybdate—Hydrazine Sulfate Solution*—Dilute 250 mL of Ammonium Molybdate Solution (20 g/L) to 600 mL, add 100 mL of Hydrazine Sulfate Solution (1.5 g/L), dilute to 1 L and mix well.

63.4 *Phosphorus Stock Solution (1 mL = 1.0 mg P)*—Transfer 2.292 g of anhydrous disodium hydrogen phosphate (Na_2HPO_4), previously dried to a constant weight at 105°C, to a 500-mL volumetric flask; dissolve in about 100 mL of water, dilute to volume, and mix.

63.5 *Phosphorus Standard A (1 mL = 0.1 mg P)*—Pipet 50 mL of Phosphorus Stock Solution into a 500-mL volumetric flask, add 50 mL of $HClO_4$(1 + 5), dilute to volume, and mix.

63.6 *Phosphorus Standard B (1 mL = 0.01 mg P)*—Pipet 10 mL of Phosphorus Stock Solution into a 1-L volumetric flask, add 100 mL of $HClO_4$(1 + 5), dilute to volume, and mix.

63.7 *Hydrochloric Acid (sp gr 1.19)*—Concentrated hydrochloric acid (HCl).

63.8 *Hydrochloric Acid (1 + 1)*—Add 100 mL of concentrated HCl to 200 mL of water and mix well.

63.9 *Hydrochloric Acid (1 + 100)*—Add 1 mL of concentrated HCl to 100 mL of water and mix well.

63.10 *Nitric Acid (sp gr 1.42)*—Concentrated nitric acid (HNO_3).

63.11 *Perchloric Acid (sp gr 1.54)*—Concentrated perchloric acid ($HClO_4$).

63.12 *Perchloric Acid (1 + 5)*—Add 100 mL of concentrated perchloric acid to 500 mL of water and mix well.

63.13 *Ferric Chloride Solution (20 g/L)*—Add 20 g of ferric chloride to a 1-L volumetric flask, add 10 mL of concentrated HCl, dilute to mark with water, and mix well.

63.14 *Ammonium Hydroxide (sp gr 0.90)*—Concentrated ammonium hydroxide (NH_4OH).

63.15 *Ammonium Chloride Solution (20 g/L)*—Add 20 g of ammonium chloride to a 1-L volumetric flask, add water, dilute to mark, and mix well.

63.16 *Sulfuric Acid (sp gr 1.84)*—Concentrated sulfuric acid (H_2SO_4).

63.17 *Sulfuric Acid (3 + 37)*—Add 30 mL of concentrated sulfuric acid to 370 mL of water and mix well.

63.18 *Sodium Sulfite.*

63.19 *Sodium Sulfite Solution (100 g/L)*—Dissolve 100 g of sodium sulfite in water, dilute to 1 L and mix.

63.20 *Hydrobromic Acid (sp gr 1.490)*—Concentrated hydrobromic acid (HBr).

63.21 *Hydrobromic Acid (1 + 4)*—Add 100 mL of concentrated HBr to 400 mL of water and mix well.

64. Hazards

64.1 See 1.3 and 1.4.

65. Preparation of Calibration Curve

65.1 *0.05–0.30 mg P/100 mL Calibration Range:*

65.1.1 Pipet 5-, 10-, 15-, 20-, 25-, and 30-mL portions of Phosphorus Standard A (1 mL = 0.1 mg *P*) into separate 100-mL volumetric flasks.

65.1.2 Add 20 mL of concentrated perchloric acid to each flask, dilute to volume, and mix well.

65.1.3 Pipet 10 mL of each solution into separate 100-mL volumetric flasks.

65.1.4 Add 15 mL of sodium sulfite (100 g/L) to each flask, swirl and gently boil the solutions for approximately 30 seconds on a hot plate in a hood.

65.1.5 Add 50 mL of ammonium molybdate-hydrazine sulfate solution to each flask and heat the flasks in a boiling-water bath for approximately 20 minutes.

65.1.6 Quickly cool the solutions in an ice bath, dilute each to 100 mL with water, and mix well.

65.1.7 Prepare a reagent blank as follows: Transfer 12 mL of $HClO_4$(1 + 5) to a 100-mL flask, then continue from 65.1.4.

65.1.8 Using water as a reference, record the absorbance of each standard solution and the reagent blank at 650 nm.

65.1.9 Prepare a calibration curve by plotting the absorbances of the standards (corrected for reagent blank) versus mg of P/100 mL of solutions.

65.2 *0.005–0.03 mg P/100 mL Calibration Range*:

65.2.1 Pipet 5-, 10-, 15-, 20-, 25-, and 30-mL portions of Phosphorus Standard B (1 mL = 0.01 mg *P*) into separate 100-mL volumetric flasks.

65.2.2 Develop the color of these standards following 65.1.2-65.1.6.

65.2.3 Prepare a reagent blank as follows: Transfer 12 mL of $HClO_4$(1 + 5) to a 100-mL flask, then continue from 65.1.4.

65.2.4 Using water as a reference, record the absorbance of each standard solution and the reagent blank at 825 nm.

65.2.5 Prepare a calibration curve by plotting the absorbances of the standards (corrected for reagent blank) versus mg of P/100 mL of solution.

66. Procedure

66.1 Weigh 1.0000 g of dried fluorspar to 0.0001 g and transfer to a 400-mL beaker. Weight = *W*.

66.2 Add 10 mL of HNO_3, 10 mL of $HClO_4$, cover the beaker with a watch glass, and heat the mixture on a hot plate. When the sample is nearly totally dissolved, remove from the hot plate, cool, then carefully wash down the watch glass and the sides of the beaker with water. Carefully evaporate the sample to near dryness on a hot plate.

66.3 Remove from heat, cool, add 10 mL of concentrated HNO_3 and 100 mL of water and heat the solution on a hot plate to dissolve the salts.

66.4 Remove the beaker from the hot plate and cool. Add 5 mL of ferric chloride solution to the beaker, then add ammonium hydroxide until iron precipitates.

66.5 Boil the solution for 3 minutes on a hot plate then gravity filter through No. 40 Whatman filter paper. Discard the filtrate.

66.6 Add 20 mL of HCl (1 + 1) to dissolve residual matter then transfer the residue to the filter, collecting the filtrate in a 250-mL Erlenmeyer flask.

66.7 Wash the beaker with 20-mL portions of hot water, transferring each wash to the filter cake. Continue the washings until there is no yellow color left on the filter paper (3–5 washings); collect all washings in the Erlenmeyer flask.

66.8 Add 10 mL of $HClO_4$ to the flask, heat on a hot plate until fumes appear, then heat one minute more.

66.9 Cool the flask, then add 20 mL of HBr (1 + 4). Heat on a hot plate until strong white fumes appear, then for one minute more.

66.10 Cool the flask, wash the contents into a 100-mL volumetric flask with water, make to volume and mix well. Pipet 20 mL of this solution into a second 100-mL volumetric flask.

66.11 Add 15 mL of sodium sulfite solution and gently boil the solution for approximately 30 seconds on a hot plate in a hood.

66.12 Add 50 mL of ammonium molybdate-hydrazine sulfate solution and heat the flask in a boiling water bath for approximately 20 minutes.

66.13 Cool the solution, dilute to 100 mL with water, and mix well.

66.14 Read the absorbance of the solution at 650 nm or 825 nm as appropriate; Absorbance = *A*.

66.15 Similarly determine the absorbance of a blank solution containing all reagents, but no sample; Absorbance = *B*.

67. Calculation

67.1 Using the calibration curves or a straight-line formula, determine the concentration of *P* in mg/100 mL equivalent to the blank-corrected absorbance (*A* − *B*); concentration = *C*.

$$P\,(\%) = \frac{C \times 100 \times 100 \times 5}{W \times 1000} = \frac{50 \times C}{W} \tag{9}$$

where:

C = mg P/100 mL, equivalent to the blank-corrected sample absorbance,
W = sample weight in g,
100 = original sample volume in mL,
100 = conversion factor to percent,
5 = dilution factor (100 mL/20 mL), and
1000 = conversion factor, milligrams to g.

68. Report

68.1 Report results to the nearest 0.001 %.

68.2 Minimum reportable quantity is 0.001 %.

69. Precision and Bias

69.1 Studies are planned to determine the precision of this test method.

69.2 The bias of this test method cannot be determined unless a suitable reference material becomes available.

ARSENIC

70. Scope

70.1 This test method covers the determination of total arsenic.

71. Summary of Test Method

71.1 The sample is oxidized with bromine and nitric acid then arsenic is determined using Graphite-Furnace Atomic Absorption Spectroscopy.

72. Apparatus

72.1 *Atomic Absorption Spectrometer*, equipped with a graphite furnace, Zeeman background correction, and an arsenic electrodeless discharge lamp.[11]

72.2 *Analytical Balance*, capable of weighing to the nearest 0.1 mg.

72.3 *Volumetric flasks*, 100-mL, 500-mL, borosilicate glass, volumetric.

72.4 *Pipets*, 1-mL, 2-mL, 10-mL.

72.5 *Phillips beaker*, 250-mL with watch glass cover.

73. Reagents

73.1 *Nitric Acid (sp gr 1.42)*—Concentrated nitric acid (HNO_3).

73.2 *Hydrochloric Acid (sp gr 1.19)*—Concentrated hydrochloric acid (HCl).

73.3 *Palladium Sponge.*

73.4 *Palladium Solution (5 g/100 mL)*—Weigh 5.0 g of Pd metal into a 250-mL beaker. Add 25 mL concentrated HCl and 25 mL concentrated HNO_3. Heat until completely dissolved. Cool, then dilute to 100 mL with water. Mix well.

73.5 *Magnesium Nitrate*—Alfa Puratronic or equivalent.

73.6 *Magnesium Nitrate Solution (1 g/100 mL)*—Dissolve 1.0 g of $Mg(NO_3)_2$ in water, then make to 100 mL. Mix well.

73.7 *Bromine/Carbon Tetrachloride (2 + 3)*—Mix 500 mL of Br_2 and 750 mL of CCl_4.

73.8 *Palladium/Magnesium Nitrate Matrix Modifier*—Dilute 6.0 mL of 5 g/100 mL Pd Solution and 10.0 mL of 1 g/100 mL $Mg(NO_3)_2$ solution to 100 mL with water and mix well.

73.9 *Arsenic Stock Solution (1000 mg/L)*—Fisher Cat. No. SA449, or equivalent.

73.10 *Arsenic Stock Solution (100 mg/L)*—Pipet 10.0 mL of 1000 mg/L Stock Solution into a 100-mL volumetric flask. Add 2 mL of concentrated HNO_3 and 10 mL of concentrated HCl and dilute to volume with water. Mix well.

73.11 *Arsenic Stock Solution (10 mg/L)*—Pipet 10.0 mL of 100 mg/L Stock Solution into a 100-mL volumetric flask. Add 2 mL of concentrated HNO_3 and dilute to volume with water. Mix well.

73.12 *Arsenic Standard Solution (1.0 mg/L)*—Pipet 10.0 mL of 10 mg/L Stock Solution into a 100-mL volumetric flask. Add 2 mL of concentrated HNO_3 and dilute to volume with water. Mix well.

73.13 *Arsenic Standard Solution (0.10 mg/L)*—Pipet 10.0 mL of 1 mg/L Standard Solution into a 100-mL volumetric flask. Add 2 mL of concentrated HNO_3 and dilute to volume with water. Mix well.

73.14 *Arsenic Standard Solution (0.01 mg/L)*—Pipet 10.0 mL of 0.10 mg/L Standard Solution into a 100-mL volumetric flask. Add 2 mL of concentrated HNO_3 and dilute to volume with water. Mix well.

74. Hazards

74.1 See 1.3 and 1.4.

75. Procedure

75.1 Weigh 0.100 g of dried fluorspar to 0.0001 g and transfer to a 250-mL Phillips beaker.

75.2 Add 10 mL of $Br_2/CCl_4(2 + 3)$, swirl to mix, cover the beaker with a watch glass, and allow to sit in a fume hood for 15 min.

75.3 Add 10 mL of HNO_3 to the sample, swirl to mix, cover, and allow the sample to sit in a fume hood for 15 min.

75.4 Heat on a hot plate at low-medium heat until brown bromine fumes are no longer visible, then continue digestion until the sample volume is approximately 5–8 mL.

75.5 Rinse down the sides of the beaker and the watch glass with approximately 50 mL of water.

75.6 Cover the sample and heat to just boiling on a hot plate. Cool.

75.7 Using water, quantitatively transfer the sample to a 100-mL volumetric flask, make to volume, and mix well.

75.8 Determine the sample's absorbance using Graphite-Furnace Atomic Absorption Spectroscopy using the following conditions:

NOTE 12—The following conditions are specific for the Perkin-Elmer equipment described in 72.1. If other equipment is used for the analysis, conditions will have to be changed appropriately.

Wavelength: 193.7 nm
Slit width: 0.7 nm
Integration time: 5 s
Lamp: Electrodeless discharge, set at 330 ma
Measurement mode: Absorbance of peak area
Gas: Argon
Zeeman background correction: On
Furnace settings:

Step	Temperature,° C	Ramp	Hold Time, s	Read
1	150	1	60	
2	400	10	30	
3	2400	0	5	X
4	2600	...	5	

75.9 Similarly determine the absorbances of a reagent blank and appropriate standards.

76. Calculation

$$\mu g/g\ (ppm\ wt/wt)\ As = \frac{A_1 \times C \times 100}{A_2 \times 0.1} = \frac{A_1 \times C \times 1000}{A_2} \tag{10}$$

where:

A_1 = blank-corrected sample absorbance,
C = concentration of standard in µg/g,
100 = sample volume in mL, and
0.1 = sample weight in g.

77. Report

77.1 Report results to the nearest 1 µg/g (ppm).

77.2 Minimum reportable quantity is 1 µg/g (ppm).

78. Precision and Bias

78.1 *Laboratory Precision (Within-Laboratory, Between-Days)*—The standard deviation of results, each the average of duplicates, obtained by the same analyst on different days, has been estimated to be 2 µg/g with 41 df. The 95 % limit for the difference between two such averages is 6 µg/g.

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[11] A system known to produce adequate results includes: a Perkin-Elmer Model PE 5000 Spectrometer and a Perkin-Elmer Model 6100 HGA Graphite Furance.

NOTE 13—This precision estimate is based on the analysis of a single sample in one laboratory over the period from May 1995 to October 1996.

78.2 The bias of this test method cannot be determined unless a suitable reference material becomes available.

MIXED OXIDES (R_2O_3)

79. Scope

79.1 This test method covers the determination of percent mixed oxides (R_2O_3).

80. Summary of Test Method

80.1 The acetic acid extract from the determination of percent silica (see 19.8) is oxidized with hydrochloric and nitric acids, then treated with ammonium hydroxide to precipitate metal hydroxides. This precipitate is combined with the ammonium hydroxide precipitate from the determination of percent calcium fluoride (see 29.17), the combined precipitates are calcined at 800°C, then the residue is weighed and calculated as percent mixed oxides (R_2O_3).

81. Apparatus

81.1 *Analytical Balance*, capable of weighing to the nearest 0.1 mg.

81.2 *Desiccator* desiccant (silica gel is suitable).

81.3 *Muffle furnace*, capable of maintaining a temperature of at least 800°C.

81.4 *Platinum crucible*, 30-mL.

81.5 *Graduated cylinders*, 10-mL, 50-mL.

82. Reagents

82.1 *Nitric Acid (sp gr 1.42)*—Concentrated nitric acid (HNO_3).

82.2 *Hydrochloric Acid (sp gr 1.19)*—Concentrated hydrochloric acid (HCl).

82.3 *Ammonium Hydroxide (sp gr 0.90)*—Concentrated ammonium hydroxide (NH_4OH).

82.4 *Filter Paper*, 9-cm, low ash, acid-washed, medium-porosity, able to retain 8-μm particles.

83. Hazards

83.1 See 1.3 and 1.4.

84. Procedure

84.1 Transfer the filtrate from the determination of percent silica (see 19.8) to a 250-mL beaker, and add 5 mL of HCl and 1 mL of HNO_3 to the beaker.

84.2 Boil the solution for 2–3 min, remove the beaker from the heat, and allow to cool.

84.3 Add 3–5 drops of 0.5 % phenolphthalein indicator solution to the sample. While stirring, add ammonium hydroxide to the solution until it turns pink, then boil the solution for one minute more.

84.4 Allow the solution to cool, then gravity filter it through medium-porosity filter paper.

84.5 Wash the filter cake with about 50 mL of hot water.

84.6 Heat a 30-mL platinum crucible at 800°C for 20 min. Cool to room temperature in a desiccator, then weigh to the nearest 0.0001 g; weight = *C*.

84.7 Combine the above filter paper and filter cake with the filter paper and filter cake from the ammonium hydroxide precipitate from the determination of percent calcium fluoride (see 29.17) in the crucible, then place the crucible in a muffle furnace and carefully ignite at 800°C.

84.8 After all the paper has burned off, heat the crucible for 5 min more.

84.9 Place the crucible in a desiccator to cool, then weigh to 0.0001 g; weight = *B*.

85. Calculation

$$\%\text{ mixed oxides } (R_2O_3) = \frac{(B - C)}{A} \times 100 \quad (11)$$

where:

B = weight of crucible plus ash, see 84.8,

C = weight of crucible, see 84.6,

A = weight of sample, see 18.2, and

100 = conversion to percent.

86. Report

86.1 Report results to the nearest 0.01 %.

86.2 Minimum reportable quantity is 0.01 %.

87. Precision and Bias

87.1 Studies are planned to determine the precision of this test method.

87.2 The bias of this test method cannot be determined unless a suitable reference material becomes available.

SULFIDE SULFUR

88. Scope

88.1 This test method covers the determination of sulfide sulfur in the range from 0.001 to 0.2 %.

89. Summary of Test Method

89.1 Fluorspar is mixed with HCl, boric acid, and amalgamated zinc. Hydrogen sulfide is then distilled from the mixture. The evolved hydrogen sulfide is carried off by a stream of oxygen-free nitrogen or argon, and collected in zinc acetate solution. Hydrochloric acid and iodine are added to the zinc acetate solution, and the excess iodine is back titrated with sodium thiosulfate.

90. Apparatus

90.1 *Analytical Balance*, capable of weighing to the nearest 1 mg.

90.2 *Sulfide Evolution Apparatus*, consisting of a nitrogen or argon gas cylinder with appropriate regulator, flow meter, gas washing bottles (250 mL), one with alkaline pyrogallol and one with zinc acetate solution (30 g/L), separatory funnel, 500-mL three-neck flask, condenser, gas washing bottle (125 mL), and connecting glass tubing (see Fig. 1).

NOTE 14—Hydrofluoric acid produced by the reaction between fluorspar and hydrochloric acid gradually corrodes the 500-mL flask. After each run, tap the bottom of the flask gently on the table top to make certain that it is still safe to use. Also, rinse down the inside of the condenser after each run to remove any globules of mercury that may be deposited there.

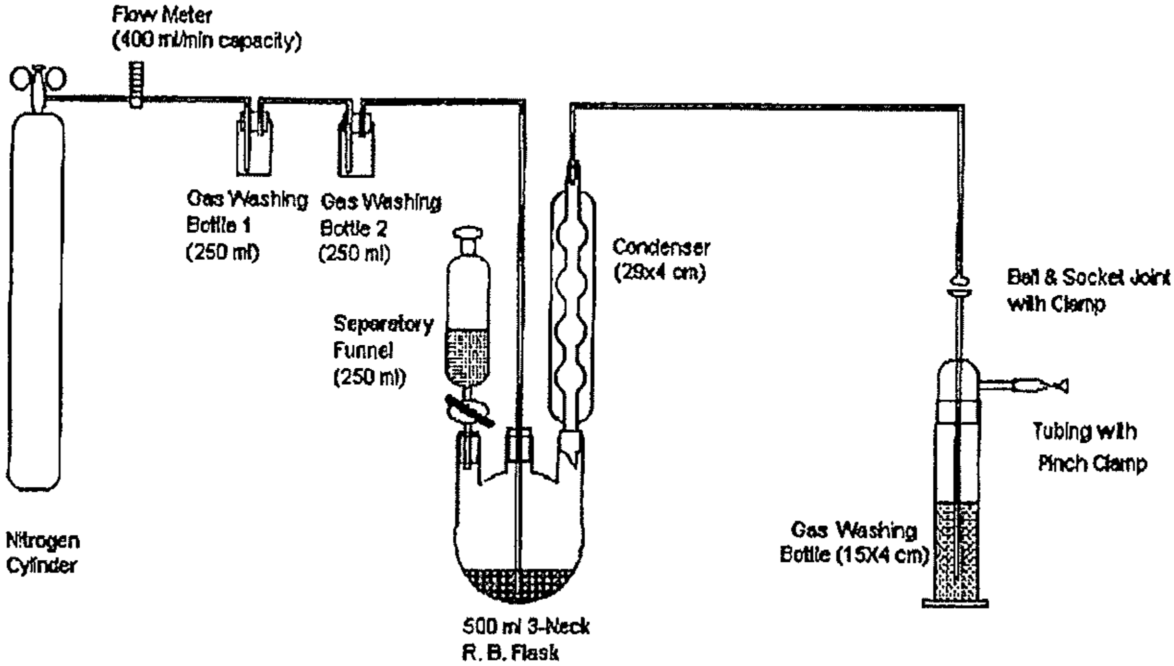

FIG. 1 Sulfide Distillation Apparatus

90.3 *Graduated Cylinder*, 100-mL, glass.

90.4 *Pipet*, 10-mL.

90.5 *Heating Mantel*, for 500-mL round-bottom flask.

90.6 *Micro-Burette*, readable to 0.01 mL.

91. Reagents

91.1 *Zinc, 20 Mesh*—Clean by treating for a few minutes with 1:19 HCl; decant off the HCl just prior to amalgamation.

91.2 *Amalgamated Zinc*—Dissolve 2 g of mercuric chloride in 50 mL of water, and add a few drops of HCl to acidify the solution. Heat to 50–60°C to dissolve any salt. Add 50 g of clean zinc to the heated solution. Allow the mixture to stand for 3 to 5 min, stirring occasionally. Pour off the supernatant liquid, and wash the zinc at least 5 times by decantation to remove excess mercuric chloride. Do Not allow the amalgamated zinc to dry. Store under water, and weigh wet.

91.3 *Hydrochloric Acid (1 + 2)*—Dilute 1 vol of concentrated HCl with 2 vol of water.

91.4 *Hydrochloric Acid (1 + 19)*—Dilute 10 vol of concentrated HCl with 190 vol of water.

91.5 *Digestion Acid*—Mix 400 mL of concentrated HCl with 1000 mL of water. Add 1 g of chromic chloride or 0.33 g of chrome metal to the solution, and mix well until the chrome dissolves.

91.6 *Boric Acid.*

91.7 *Starch Solution*, 1 %.

91.8 *Nitrogen or Argon*, oxygen-free.

91.9 *Iodine, 0.005 N*—Prepare fresh. Pipet 10 mL of standard 0.1 N iodine to 200 mL with water, and mix well.

91.10 *Zinc Acetate Solution (30 g/L)*—Dissolve 30 g of zinc acetate and 6 mL of glacial acetic acid in water and dilute to 1000 mL.

91.11 *Sodium Thiosulfate, Standard Solution (0.01 N)*—Prepare fresh. Pipet 20 mL of standard 0.1 N sodium thiosulfate solution into a 200-mL volumetric flask, dilute to the mark with water, and mix well.

91.12 *Alkaline Pyrogallol*—Add 50 mL of 10 % aqueous Pyrogallol to 200 mL of 50 % weight/vol aqueous KOH. Mix well. Store in a tightly-capped container until used.

92. Hazards

92.1 See 1.3 and 1.4.

93. Procedure

93.1 Assemble the apparatus shown in Fig. 1, making certain that all Teflon® stoppers and connections are tight.

NOTE 15—The apparatus operates under a slight positive pressure, and therefore, all connections must be tight. Even a small leak may result in a serious loss of hydrogen sulfide.

93.2 Place 50 mL of zinc acetate solution into the gas washing bottle.

93.3 Weigh 3 g of dried sample to the nearest 0.001 g, and transfer it to the 500-mL three-neck flask; record the sample weight as *A*.

93.4 Add 2.5 g of amalgamated zinc and 2 g of boric acid to the flask.

93.5 Connect the flask to the gas train, and with the pinch clamp open, adjust the nitrogen flow to about 100 mL/min, and purge the apparatus for 10 min.

93.6 Add 85 mL of digestion acid to the separatory funnel.

93.7 Open the separatory funnel stop cock. Using a pipet bulb, force about 80 mL of the acid into the 500-mL flask, making certain that no air enters the flask. Close the stop cock.

93.8 Boil the contents of the flask for 30 min, adjusting the temperature so that froth about half-fills the flask, but does not rise high enough to enter the neck of the flask.

93.9 Carefully disconnect the delivery tube from the condenser, at the ball and socket joint, and seal the outlet tube on the gas washing bottle with tubing and a clamp.

93.10 Remove cap from gas washing bottle. Quickly add 10.0 mL of 0.005 N iodine solution and 10 mL of HCl (1+2) solution to the zinc acetate collection solution in the gas washing bottle. Replace cap. Keeping the outlet tube sealed, allow the mixture to stand for about 15 min.

93.11 Remove cap, open pinch clamp, and rinse the gas inlet tube carefully, collecting the washings in the bottle. Take care that all the zinc sulfide adhering to the inlet tube has been dissolved completely.

93.12 Using 0.005 N sodium thiosulfate, back-titrate the excess iodine, adding 1 mL of starch solution just before the end-point is reached. Continue titrating to the clear end-point. Record *B*, the millilitres of 0.005 N sodium thiosulfate needed for the titration.

93.13 Similarly, determine a blank, using all of the same reagents, but no sample. Record *C*, the millilitres of 0.005 N sodium thiosulfate needed for the blank.

94. Calculation

94.1 Calculate:

$$\%\ \text{sulfide sulfur} = \frac{(C - B) \times N \times 0.016 \times 100}{A} \tag{12}$$

where:

B = sodium thiosulfate used for the sample, mL,
C = sodium thiosulfate used for the blank, mL,
A = sample weight, g,
0.016 = milliequivalent weight of sulfur, and
N = normality of sodium thiosulfate.

95. Report

95.1 Report the concentration of sulfide sulfur to the nearest 0.0001 %.

95.2 Minimum reportable quantity is 0.0001 %.

96. Precision and Bias

96.1 *Laboratory Precision (Within-Laboratory, Between-Days)*—The standard deviation of results, each the average of duplicates, obtained by the same analyst on different days, has been estimated to be 0.0003 % with 17 df. The 95 % limit for the difference between two such averages is 0.0008 %.

NOTE 16—This precision estimate is based on the analysis of a single sample in one laboratory over the period from April to October 1996.

96.2 *Bias*—The bias of this test method cannot be determined unless a suitable reference material becomes available.

97. Keywords

97.1 arsenic; calcium carbonate; calcium fluoride; fluorspar; mixed oxides (R_2O_3); moisture; phosphorus; silica; soluble chloride; sulfide sulfur; volatiles

APPENDIX 3:
DELTA MINERALS PTY LTD, JUNE 2007 –
FLUORSPAR FLOTATION TESTWORK
REQUIREMENTS

MINEMAKERS LIMITED

and

WOLFRAM BERGBAU und HÜTTEN GmbH Nfg.KG

MOINA PROJECT, TASMANIA

PROPOSAL FOR EXPLORATORY LABORATORY TESTWORK AT MITTERSILL

July 2007
Draft Edition for Consideration

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TABLE OF CONTENTS

1.0 BACKGROUND

- Minemakers Limited and Wolfram Bergbau und Hütten Gmbh Nfg.KG (WBH) have signed a Memorandum of Understanding to co-operate in the development of tungsten and tin resources in Tasmania.

- The Moina area of Tasmania is known for its tungsten and tin mining history. In the 1970s, well after the closure of previous mining activities, testwork was undertaken on samples of drill core from the orebody. Despite the multi-mineral content, including fluorspar, magnetite, scheelite, tin, copper, zinc, bismuth, molybdenum, gold, and garnet, the respective recoveries and grades were poor due to their fine liberation sizes and consequently the results failed to justify development of the orebody.

- WBH has agreed to carry out exploratory testwork on fresh samples of drill core, firstly to verify the previous results and, secondly, by using modern techniques and reagents, to attempt to improve the recoveries and grades of the primary values, i.e. fluorspar, scheelite, tin, bismuth, and sulphides.

- WBH is considered to be a leader in tungsten beneficiation and refining and Delta Minerals Limited, a specialised consultant to the fluorspar industry, has agreed to assist in all areas of the testwork related to fluorspar and fluorite/scheelite selectivity.

- Delta Minerals has agreed to draft an outline proposal for the exploratory testwork programme for discussion and fine-tuning by WBH and Minemakers, after which the final version will set the scope for the testwork to commence and act as a reference template during the programme.

2.0 OBJECTIVES OF THE TESTWORK

The scope and objectives for the testwork programme were broadly defined by Andrew Drummond in his letter dated 12th June 2007. These have been expanded as follows:

2.1 Primary Objectives

- To verify the past recoveries and grades of the primary mineral values, i.e. fluorspar, scheelite, tin, bismuth, and sulphides, and re-confirm that the beneficiation of the ore is not technically or economically fatally flawed.
- To improve on the 1970s recoveries and grades through the use of modern techniques and reagents, while limiting the programme to the minimum possible number of tests at exploratory level. Each testwork phase will therefore not be optimised.
- To demonstrate whether commercially acceptable grades of concentrate for each valuable mineral can be achieved at a recovery considered likely to be viable at this early stage.

2.2 Secondary Objectives

- Assuming that beneficiation of the ore is found likely to be viable, to propose a likely processing route.
- To expose any potential processing pitfalls, thereby giving a future pre-feasibility study a head-start.

3.0 SCOPE OF WORK

The testwork programme has been divided into nine separate phases:

3.1 Phase I - Sample Preparation and Physical Examination

- Receiving and laying out the drill core samples.
- Crushing and compositing set intervals of drill core, the length of interval depending of the total amount of core.
- Assaying each interval.
- Preparation of equal composites from the combination of all intervals, to provide sufficient bulk sample for all phases of testwork. Any excess sample to be placed in storage.

3.2 Phase II – Mineralogical and Liberation Examination

- Preparation of a representative split from the bulk sample into a series of up to five particle size fractions within the range 150 µm to 38 µm.
- Preparation of polished sections and thin sections for optical microscopy using incident and transmitted light to confirm the identification of the value minerals, their liberation character, and their associated minerals within binary and complex particles.
- Ore mineralogy of the same size fractions under a binocular microscope using both standard light and ultraviolet light.

3.3 Phase III – Primary Grinding Tests

- Timed grinding tests to prepare samples for gravity separation of coarse liberated scheelite, and possibly small amounts of the other heavy minerals. Past results indicated that the scheelite is mainly liberated at +63 µm, but none of the other heavy minerals were significantly liberated above 38 µm.

3.4 Phase IV - Gravity Separation of +63 µm Scheelite

- Gravity testwork with the most suitable equipment available at lab-scale for recovery of scheelite down to 63 µm.

- Investigate the possibility of preparing a magnetite gravity concentrate without major losses of fluorite. Previous testwork indicated that magnetic separation always resulted in excessive fluorspar losses, but there would be a major advantage if most of the liberated magnetite could be removed prior to regrinding.

3.5 Phase V - Regrind Tests

- Timed grinding tests to prepare gravity tailings samples for flotation. The 1970s testwork indicated that regrinding to 17 µm will be necessary, but this will be subject to verification during the liberation examination. Subject to this verification, re-grinding to 80% passing 17 µm appears likely.

3.6 Phase VI - De-sliming at 5 µm

- Due to the very fine grind, there is a risk that some of the gangue minerals, especially the biotite, will form fine slimes which will have a strong negative impact on flotation. As a precaution, the reground product should be de-slimed at 5 µm, either in bulk using a 25 mm cyclone or on a batch basis by settling and siphoning.

3.7 Phase VII - Sulphide Flotation

- Bulk sulphide flotation tests using a strong xanthate such as potassium amyl xanthate, with the twin objectives of firstly removing all the sulphide sulphur content which will contaminate the fluorspar concentrate and secondly producing a saleable sulphide concentrate.

3.8 Phase VIII – Tin Flotation

- Although the liberation size of the cassiterite is less than 10 µm, it would be worth attempting several tin flotation tests at acid pH using a phosphonic acid collector such as styrene phosphonic acid in the presence of sodium silicate and sodium fluoride.

3.9 Phase IX - Flotation of Scheelite and Fluorite

- In order to float the scheelite, the fluorite must be depressed using a high dosage of sodium silicate at high pH.

- The reagent dosages and the pH are sensitive and there is only a small range of conditions at which selectivity between the WO_3 and CaF_2 can be achieved, especially at such a fine particle size. There will therefore be a need to carry out a number of tests to locate the conditions close to the zone of selectivity.

- By lowering the pH, activating the fluorspar, and depressing the gangue minerals, the fluorspar can then be floated using a separate collector.

- If a lab column cell is available, this would give superior results to a standard bench agitator cell due to the extremely fine particle size of the feed.

- Up to six stages of cleaning will be required to raise the concentrate grade to acidgrade specification. Past testwork revealed that the fine association between fluorite and magnetite or silica prevented acidgrade fluorspar from being achieved at a viable recovery. Therefore it is envisaged that the cleaned concentrate may assay only 95% CaF_2 and specific markets would be created for this quality of product.

- Analysis of CaF_2 is particularly troublesome at grades over 75% CaF_2 and, well in advance of Phase IX, there will be a need to establish the precise method of analysis for CaF_2 in feed, concentrate and tailings samples.

4.0 TESTWORK SCHEDULE

The timing for the start of the testwork programme and the precise schedule for the separate phases will be determined by Wolfram Bernhart who will also be responsible for the overall management. The details of the schedule and the allocation of WBH lab technicians will be advised after the scope of work has been finalised. The analytical turn-around time for sample assays will play a major role in the testwork schedule. After fine-tuning the scope of work and completing Phases I and II, Malcolm Crawford of Delta Minerals will meet Wolfram Bernhart at the lab at Mittersill to discuss the mineralogical results and re-evaluate the remaining phases with the aim of minimising the total number of tests required. As soon as the programme approaches Phase IX, Malcolm Crawford will re-visit Mittersill to assist with the initial scheelite and fluorspar flotation tests where the selectivity between scheelite and fluorite is likely to be challenging.

WBH already has extensive experience in the treatment of tungsten ores, therefore this proposal reflects the need for Delta Minerals to focus only on the beneficiation of the fluorspar and the interfaces with scheelite. Based on the commendable success of the 1970s results from only nine bench tests, it is estimated that Phase IX will require 20 to 30 flotation tests to meet the testwork programme objectives. The previous phases will require only a small number of tests (probably less than 10). The total number of tests will always be trimmed to the minimum, and the schedule should remain flexible throughout, to cater for unexpected results.

5.0 ADVANCE PREPARATION

Past experience from other similar projects involving the selective flotation of scheelite and fluorite has demonstrated that the task will be challenging, especially at such fine particle sizes. The similar surface characteristics of these two calcium minerals will require highly specific depression and activation conditions to achieve selectivity, and it is likely that two separate collectors will be required. In preparation for Phase IX, the following flotation reagents should be obtained:

Reagent Type	**Name**	**Composition/Brand**
pH Modifier	Soda Ash	Na_2CO_3
pH Modifier	Caustic Soda	NaOH
pH Modifier	Sulphuric Acid	H_2SO_4
Selectivity Agent	Sodium Silicate	Na_2SiO_3
Selectivity Agent	Tannin	Unitan
Selectivity Agent	Tannin	Tupasol
Selectivity Agent	Tannin	Tan-X
Selectivity Agent	Sodium Fluoride	NaF
Collector	Oleic Acid Mixture	Flotinor FS-2
Collector	Oleic Acid Mixture	Sylfat FA2
Collector	Oleic Acid Mixture	Oleoflot R33F

If required, it may be possible for Delta Minerals to obtain small lab samples of the tannin depressants from other projects and have them sent by courier to Mittersill.

6.0 CONCLUDING REMARKS

The primary reason that the Moina orebody has remained undeveloped is due to the complex nature of the finely associated mineral values and the corresponding impact on beneficiation. It should therefore come as no surprise that these exploratory tests will be challenging, and initial grades and recoveries are likely to be disappointingly low. Column cells are likely to be the key to improved results over those achieved in the past, and if WBH has a lab-scale column, this will be a great advantage. Past experience has demonstrated that scheelite recovery will be maximised by removing as much of the liberated +63 µm scheelite as possible by gravity separation prior to flotation of the remaining fine scheelite ahead of the fluorspar flotation circuit.