Guidelines for Landfill Disposal of Sulphur Waste and Remediation of Sulphur Containing Soils

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Table of Contents

Pre	eface	iii
Abl	breviations	iv
Def	finitions	V
1.	Introduction	1
2.	Legislation	3
3.	Approvals Required	7
4.	Effects of Sulphur on Soil	9
	4.1 Neutralization with Alkaline Products	9
	4.2 Alternative Alkaline Products	10
5.	What Is Sulphur Waste?	11
	5.1 Classification of Sulphur Waste	11
	5.2 Neutralization of Sulphur Waste (or Sulphur Containing Soil)	12
	5.3 Beneficial Use of Sulphur Waste	13
6	Landfill Disposal of Sulphur Waste	15
	6.1 Small Quantities of Sulphur Waste	16
	6.2 Large Quantities of Sulphur Waste	
	6.3 Monitoring	20
7	Remediation of Sulphur Containing Soil	21
	7.1 In Situ Land Remediation	21
	7.2 Land Application	22
	7.3 Soil and Water Monitoring	23
8	Test Methods, Record Keeping, and Reporting	
	FERENCES	
AP	PENDIX 1: RECOMMENDED TEST METHODS	29
AP	PENDIX 2: FREQUENTLY ASKED QUESTIONS	31
APPENDIX 3: EXAMPLES		

Preface

These Guidelines for the Disposal of Sulphur Waste and the Remediation of Sulphur Containing Soils (the Guidelines) amend, consolidate, and replace the Guidelines for the Disposal of Sulphur Containing Solid Waste (1983) and the Guidelines for the Remediation and Disposal of Sulphur Contaminated Wastes (1996) published by Alberta Environment. Significant parts of these two documents have been incorporated with changes into these Guidelines which are to be effective September 12, 2011.

These *Guidelines* do not apply to the production, recovery, processing or storage of sulphur as a product. Instead, they are restricted to and provide information on acceptable industry practices regarding the management of sulphur waste and sulphur containing soils incidental to those activities.

If there is a conflict between these *Guidelines* and the *Environmental Protection and Enhancement Act*, the *Oil and Gas Conservation Act*, the *Oil Sands Conservation Act* or their *Regulations*, specific approvals or authorizations, which may contain more stringent requirements, then the legislation or the AENV or ERCB approvals take precedence over the *Guidelines*. For a comprehensive review of Alberta's waste legislation review the documents identified in section 2.

AENV and ERCB staff are available to clarify policy and legislation in case of doubt, but it is the responsibility of the persons responsible to satisfy themselves as to the proper interpretation of these *Guidelines* if they are uncertain. Responsibility for proper sulphur waste disposal and the remediation of sulphur containing soils rests with the person responsible, despite anything written in these *Guidelines*.

Abbreviations

AENV Alberta Environment

CCE Calcium carbonate equivalent

EPEA Environmental Protection and Enhancement Act

ERCB Energy Resources Conservation Board

Guidelines Guidelines for the Landfill Disposal of Sulphur Waste and the

Remediation of Sulphur Containing Soils

ID Interim Directive

IL Information Letter

MSDS Material Safety Data Sheet

MOU Memorandum of Understanding

OGCA Oil and Gas Conservation Act

OSCA Oil Sands Conservation Act

S Symbol for sulphur

User Guide Alberta User Guide for Waste Managers, 1995

WCR Waste Control Regulation

Definitions

All definitions in the *EPEA*, *OGCA* and their *Regulations* apply to these *Guidelines*. The following additional definitions are included here for comprehensiveness, interpretation or clarification of the meaning of the terms used in this document.

- (a) "3/8ths minus" means lime, limestone or equivalent product for which a sieve analysis shows that 20% of the product passes a 60 mesh sieve, 60% passes a 10 mesh sieve, and 100% passes a 3/8" sieve.
- (b) "Acid neutralizing capacity" or "ANC' means the ability of a substance to neutralize an acidic material. It is measured by a titration method such as AOAC 955.01. Although the results are often expressed as the calcium carbonate equivalent, the titration method measures all acid neutralizing compounds, not just carbonate.
- (c) "Alkaline product" means limestone, lime or an alternative alkaline product derived from waste with a MSDS that identifies the waste as a suitable neutralizing or buffer alkaline material when remediating S-containing soils or mixing with and/or encapsulating S-waste at landfills.
- (d) "ERCB facility" means an upstream oil and gas facility approved by the ERCB and as defined in the *Oil and Gas Conservation Act*. The *OGCA* is found at http://www.qp.alberta.ca/.
- (e) "Landfill" means a waste management facility at which waste is disposed of by placing it on or in land, but does not include a land treatment facility, a surface impoundment pond, a salt cavern or a disposal well.
- (f) "Large quantity" means, for the purpose of this document, a quantity of S-waste that exceeds a truck load or 10 cubic meters or 20 tonnes per calendar month or landfill disposal event. (Note: Multiple loads of small quantities of S-waste produced by the same generator are considered for landfill disposal purposes a large quantity when disposed of at the same dedicated landfill cell and may follow the alternating method of disposal described in section 6.2.)
- (g) "Lime" means 'quicklime' or 'hydrated lime' which are products derived from limestone.
- (h) "Limestone" means a naturally occurring sedimentary rock consisting primarily of calcium carbonate.
- (i) "MSDS" means a Material Safety Data Sheet prepared as required by the *Hazardous Products Act* (Canada). The MSDS identifies the product, origin, uses, physical/chemical properties, precautions and procedures when used, and disposal methods for when it becomes a waste.
- (j) "Off-specification" or "off-spec" product or material means that the product or material does not meet the quality standards required to satisfy its designed

purpose or its Material Safety Data Sheet (MSDS).

- (k) "Oilfield waste" means an unwanted substance or mixture of substances that results from the construction, operation, abandonment or reclamation of a facility, well site or pipeline as defined in the OGCA and its Regulations, but does not include an unwanted substance or mixture of substances from such a source that is received for storage, treatment, disposal or recycling at a facility authorized for that activity under EPEA.
- (I) "Oilfield waste management facility" means a facility approved by the ERCB under the OGCA and its Regulations to process, treat, store, dispose or recycle oilfield waste.
- (m) "S" is the chemical symbol for elemental sulphur. Is often used throughout the Guidelines as an abbreviation for "sulphur".
- (n) "SO₄" stands for sulphate(s) in wastes, soils, or products.
- (o) "Small quantity" means, for the purpose of this document, a quantity of waste that does not exceed a truck load or 10 cubic meters or 20 tonnes per month or landfill disposal event.
- (p) "Sulphur containing soil" means in-situ or excavated soil that contains sulphur (in an elemental and/or reduced form).
- (q) "Sulphur manufacturing or processing plant" means a facility that manufactures or processes compounds containing elemental sulphur in a quantity greater than 1.0 tonne per day.
- (r) "Sulphur storage facility" means a facility that has a storage capacity for S of greater than 100 tonnes of S.
- (s) "Sulphur waste" or "S-waste" means waste that contains S in a reduced and/or elemental form in excess of 500 milligrams of sulphur per kilogram of waste or soil and that is intended to be disposed of.

¹ Sulphur manufacturing or processing and sulphur storage are activities mostly associated with hydrocarbon processing and sulphur recovery plants and that require an EPEA and/or OGCA approval. ERCB ID 2001-3 Sulphur Recovery Guidelines for the Province of Alberta available at http://www.ercb.ca/ also apply to these activities.

1. Introduction

Canada, with a production of about 9 million tonnes per year, is the world's second largest producer of sulphur (S), a valuable by-product of Alberta's oil and gas industry. Because the generation of S-waste is incidental to the production, recovery, processing or storage of S as a resource or product, regional plans, policies or strategies affecting those activities may influence the management of S-waste. Regardless, these *Guidelines* are not applicable to S as a product. Instead, their objective is to describe procedures and recommendations required for the proper management of S-waste and the remediation of S containing soil.

Small quantities of S-waste are produced when S is removed from natural gas, crude oil, and hydrocarbon products and includes, without limitation, spent sweetening agents, used catalysts, and S-contaminated debris, soil or industrial equipment. Large quantities of S-waste result from railway car accidents, the reclamation of S-block storage areas, and off-specification S or residues from S production, storage, and recovery processes.

These *Guidelines* do not apply to the management of wastes containing S in an oxidized form such as gypsum from fertilizer manufacturing plants or from scrubbing SOx from gas stacks. This includes wastes with sulphates (SO_4^{2-}) or sulphites (SO_3^{2-}) because the S present in those wastes can not be further oxidized to produce sulphuric acid.

Though S recovery is the primary driver in dealing with S-waste and S-containing soils, in situ land treatment and land application to S-deficient soils as a fertilizer should be used whenever possible with landfill disposal of S-waste being the last resort and used only when other options are inappropriate.

The landfill disposal of S-waste and the remediation of S-containing soil must be done in compliance with the *Waste Control Regulation* and/or *Directive 58*, as applicable, and the recommendation and procedures outlined in these *Guidelines*

The *Guidelines* emphasize the addition of suitable alkaline buffer products to the affected soil or waste in order to minimize adverse environmental impacts, and their ultimate objective is to eliminate the environmental liability that may result from the improper landfill disposal of S-waste or the deficient remediation of S-contaminated land. Specific objectives of the Guidelines are to ensure that the person responsible adopts sound procedures that result in:

- controlling the rate of sulphur oxidation;
- neutralizing any free sulphuric acid eventually formed; and
- preventing the formation of acidic leachate from sulphur cell/trenches.

2. Legislation

Persons responsible for the management of S-waste and/or S contaminated land should be familiar with Alberta's waste related legislation. The most relevant regulatory documents are identified below. All Alberta's legislation is available at http://www.gp.alberta.ca.

S-waste including excavated S-containing soil is an oilfield waste when it results from the processing of hydrocarbons or recovery of S at upstream oil and gas facilities approved by the ERCB pursuant to the *OGCA*. Oilfield wastes directed to facilities authorized by AENV are, upon acceptance at these facilities, regulated under *EPEA* and associated regulations, namely the *WCR* and the *ADR*.

- Environmental Protection and Enhancement Act (EPEA) RSA 2000, Chapter E-12, Current as of November 1, 2010
 - Section 176 of the Act requires disposal of waste at approved waste management facilities or as authorized in writing by the Director.
- Activities Designation Regulation (ADR) AR 276/2003 with amendments up to and including AR 97/2011
 - Sections 2 and 3 on definitions for landfill, land treatment, oilfield waste, waste, sulphur manufacturing or processing plant, and sulphur storage facility.
 - Section 5 on the designation of activities and approvals required.
 - Section 6 empowers the Director to issue combined or individual approvals or registrations where more than one activity takes place at one particular site, as appropriate.
 - Schedule 1, Division 1, clause (i) identifies a landfill as a facility that requires approval under the EPEA.
 - Schedule 2, Division 1, clauses (a) and (c) identify land treatment and landfill disposal as activities that require EPEA registration.
- Waste Control Regulation (WCR) AR 192/1996 with amendments up to and including AR 68/2008
 - o Section 1 on definitions such as recyclable, oilfield waste, waste.
 - Sections 13(2)(c) and 23(1) on landfill disposal prohibitions.
- Alberta User Guide for Waste Managers, 1995 (User Guide)
 - o Part 1A, pgs 21-23, things that are not hazardous waste
- Release Reporting Regulation (RRR) AR 117/1993 with amendments up to and including AR 386/2003

- Substance Release Regulation (SRR) AR 124/1993 with amendments up to and including AR 114/2006
- Oil and Gas Conservation Act (OGCA) and Regulations RSA 2000, Chapter O-6, as of December 2, 2010. Waste produced by a facility as defined in the OGCA and its Regulations is defined as oilfield waste and regulated by the ERCB.

Management requirements for oilfield waste are set out in Directive 58: Oilfield Waste Management Requirements for the Upstream Petroleum Industry, as amended. Further guidance is in ID 2000-3: Harmonization of Waste Management, ID 2000-4: An Update to the Requirements for the Appropriate Management of Oilfield Wastes, and ID 99-4: Deposition of Oilfield Waste into Landfills.

Provided that the management of *oilfield waste* meets the ERCB requirements, further guidance specific to the management of S-waste is found in these *Guidelines*.

- ERCB directives, information letters (IL), interim directives (ID), and directives are available at URL http://www.ercb.ca/portal/server.pt.
 - o **Directive 58,** Oilfield Waste Management Requirements for the Upstream Petroleum Industry. (November 1996, addendum added December 23, 2008)
 - Directive 47, Waste Reporting Requirements for Oilfield Waste Management Facilities (February 13, 2009 - effective April 1, 2009)
 - o **ID 2000-4,** An Update to the Requirements for the Appropriate Management of Oilfield Wastes (ERCB). Prohibits most oilfield wastes, including S-wastes, from disposal at *EPEA* registered Class II landfills.
 - ID 2003-3, MOU on the Harmonization of Waste Management clarifies ERCB and AENV jurisdictional roles.
 - ID 99-4, MOU on the Deposition of Oilfield Waste into Class II Landfills identifies waste quality and landfill design requirements for specific oilfield wastes disposal at Class II landfills.
 - IL 84-11, Approval, Monitoring, and Control of Sulphur Storage Sites.
 Summarizes the responsibilities of the ERCB and AENV and guidelines for S production and handling facilities.
- Oil Sands Conservation Act provides authority for the approval of oil sands processing plants and associated S recovery facilities.

• Transportation of Dangerous Goods Regulations (TDGR).

TDGR identifies solid and molten sulphur as Class 4.1 dangerous goods when transported as a solid or a liquid with the product identification number UN 1350 or UN 2448, respectively, packing Group III. Depending on the transportation, some exemptions apply. Spent iron sponge, which contains iron oxide, a substance prone to spontaneous combustion, is a Class 4.2 dangerous good with a PIN UN 1376, Packing Group III. Additional information on TDGR rules is available at (780) 422 9600 or 1 800 272 9600.

Occupational Health and Safety Act.

Due to the presence of high percentages of S, some S-wastes are flammable and as such also regulated as a *controlled product* under the *Hazardous Products Act* (Canada) as it relates to workers' occupational health and safety. Employers must ensure proper labeling of controlled products, and provide workers who handle flammable S and S-waste with adequate education and training to ensure that their health and safety are protected. Detail on applicable requirements at http://employment.alberta.ca/documents/WHS/WHS-PUB ch044.pdf.

3. Approvals Required

The ERCB and AENV encourage persons responsible for the management of S-waste to consider waste prevention or recovery before disposal. S as a by-product of the oil and gas industry sector should always be managed as a resource. In that regard, the approvals required for the production, processing, and storage of S are identified in the ADR and ERCB information Letter 84-11 pursuant to EPEA and the OGCA, respectively.

The landfill disposal of S-waste and the remediation of S-containing soils are activities that per se do not require additional specific approvals under *EPEA* or the *OGCA*. Generally, the ERCB or AENV regulations, approvals, authorizations and guidance documents include provisions applicable to the management of S-waste and the remediation of S-containing soils. If not, those regulatory documents are complemented by what is described in these *Guidelines* to ensure accountability in dealing with these wastes or soils.

3.1 Landfill Disposal of S-waste

Landfill disposal of S-waste is limited to AENV or ERCB approved Class I or Class II landfills. These facilities may be located at S production or recovery plants, within mined out areas at coal and oil sands plants or off-site as stand alone or components of specific waste management facilities.

Prior to receiving S-waste for disposal, the existing approval must contain provisions relevant to the landfill handling and disposal of S-waste (see Appendix 2). Otherwise, the approval holder must contact the AENV regional office to determine if specific authorizations are required.

AENV registered Class II landfills operating under the Code of Practice for Landfills are restricted to disposal of <u>small quantities</u> of <u>non-oilfield</u> S-waste provided that the S-waste is not co-disposed with MSW; the disposal meets section 6.1(a) to (f) of these <u>Guidelines</u>. Acceptance of large quantities or multiple loads of small quantities will require prior written authorization from AENV. A Class II registered landfill is a landfill where not more than 10 000 tonnes per year of waste is disposed of.

Regardless of the approval, the class and design of the landfill, and the quantity of S-waste disposed of, the applicable disposal procedures must be described in the landfill operations plan, specifically, or by reference to the appropriate sections of these *Guidelines*. In all cases, the person responsible for the S-waste must obtain prior permission from the landfill operator before shipping the S-waste off-site for landfill disposal.

3.2 Remediation of S-containing soils

The *in-situ remediation* of S-containing soil or the *land application* of S products derived from waste to S-deficient soils must be conducted in compliance with the technical procedures identified in section 7 of these *Guidelines*.

The person responsible for the application to land of any *oilfield waste* (including Swaste or alkaline wastes) generated as a result of oil and gas activity must meet the requirements set out in Directive 58.

4. Effects of Sulphur on Soil

Under aerobic conditions, specific micro-organisms may oxidize the S in wastes, water or soil through the reaction:

$$S + 3/2O_2 + H_2O \rightarrow H_2SO_4$$
 (induced by bacterial action)

Sulphuric acid increases soil acidity, solubilizes sulphates, mobilizes trace metals from soil, reduces the concentration of basic ions, decreases soil availability of nutrients, and ultimately reduces microbial activity. Acid neutralizing agents such as limestone (a mixture of calcium and magnesium carbonates), hydrated lime (calcium hydroxide), quick lime (calcium oxide) or equivalent alkaline products are suitable to buffer or mitigate these effects and should be used when remediating S-containing soils or landfilling S-wastes.

Limestone is recommended for *in situ* land remediation and land application of S impacted soils and landfill disposal of S-wastes. Hydrated lime or quicklime (commonly known as 'lime') is suitable for treatment of S-affected soils or disposal with S-waste but its use in land application or *in situ* treatment requires planning of frequency and application rates because it can raise soil pH above the levels that are optimum for agricultural and forestry production.

Strong bases must not be used in S-waste land management programs because they contain soluble salts which may have adverse effects on the structure of soils and clay landfill liners. Alternative alkaline materials derived from wastes might be suitable but only upon assessment on a case-by-case basis to evaluate the suitability of the candidate alternative material including without limitation the acid neutralizing capacity (often expressed as the calcium carbonate equivalent) of the material, its constituents, contaminants present and concentrations, and the potential impacts.

4.1 Neutralization with Alkaline Products

The neutralization of sulphuric acid with limestone or hydrated lime involves the following reactions:

Calcium Carbonate (limestone) Weight ratio
$$H_2SO_4 + CaCO_3 \rightarrow CaSO_4 + CO_2 + H_2O$$
 (1) $CaCO_3/S = 3.2$ Hydrated Lime $H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2H_2O$ (2) $Ca(OH)_2/S = 2.4$

Gypsum (calcium sulfate dihydrate or CaSO₄.2H₂O) is only slightly soluble in water and soil salinity problems are unlikely to occur. However, limestone often contains magnesium carbonate (MgCO₃) which within an acidic environment produces soluble magnesium sulphate that can adversely affect soil and water quality because of increased salinity. Consequently, when limestone is used to remediate S-containing soils, the MgCO₃ content shall not exceed 2%.

More generally, the weight ratios identified above apply to pure limestone or pure lime, e.g. when 100% calcium carbonate or 100% lime are used to remediate S-containing soil or when are mixed with S-waste. In summary, both the quantity in kilograms and the thickness in metres of the layers of the alkaline products identified in 6.1 and 6.2 should be adjusted to reflect:

- (a) the actual acid neutralizing capacity (ANC), often expressed as the calcium carbonate equivalent of the alkaline product; and
- (b) the buffer capacity (again the ANC), if any, of the S-waste or S-containing soil being disposed or remediated, respectively.

4.2 Alternative Alkaline Products

The use of alkaline products other than the pure products indicated in 4.1 to neutralize S-waste requires the person responsible for the alternative alkaline product to carefully evaluate the product including without limitation the following:

- (a) the ANC (often expressed as calcium carbonate equivalent) of the candidate alkaline product;
- (b) information on the product necessary to prepare a MSDS;
- (c) identification of the weight and volume and/or thickness needed to neutralize or buffer the S-waste or S containing soil, as applicable;
- (d) identification of any constituent, contaminant, moisture and conditions that may limit its use; and
- (e) any mitigative measures as required by (d).

Alternative products may include quick lime, by-product or spent lime, cement kiln dust, crushed concrete, fly and bottom ashes, etc. Each candidate product should be assessed on its own merits. For instance, quick lime (CaO) should not be used for safety reasons unless it is previously reacted with water under controlled conditions. This reaction is highly exothermic and the heat released together with the pyrophoric nature of some S-wastes makes it highly incompatible.

The generator of alkaline products derived from waste shall develop an MSDS and provide a copy to the receiver/user of the alkaline product

The intent of this case-by-case evaluation is to ensure that the alternative alkaline product is suitable and equivalent in effectiveness to the stoichiometric quantities of the pure products indicated in 4.1. For instance, specific fossil fuel ashes might not be appropriate due to the high content of certain heavy metals and thus the likelihood of these being leached out and pollute the environment.

5. What Is Sulphur Waste?

Sulphur waste includes without limitation the following:

- (a) spent sweetening agents containing elemental S and sulphides;
- (b) spent catalysts from S production, recovery or desulphurization plants;
- (c) industrial equipment or materials impregnated or covered with S scaling or incrustations;
- (e) S contaminated with hydrocarbons, methanol, glycol, amines, etc.;
- (f) S contaminated soil from S spills;
- (g) S contaminated materials or debris;
- (h) off-specification S, unrecoverable S, or contaminated S from S production, processing, recovery or storage;
- (i) contaminated S soil or material removed from S production, processing, recovery plants, S-block base pads, and/or storage areas;
- (j) S-containing soil or material from the remediation of S contaminated sites; or
- (k) contaminated S from transport accidents.

Spent sweetening agents such as iron sponge [which contains pyrite (FeS₂), troilite (FeS) and elemental S] are easily oxidized with the release of heat. To dissipate the heat from this exothermic reaction and prevent fire during and upon removal of the spent material from absorption towers, S pyrophoric wastes should be kept moist when handled and within an oxygen-starved environment.

If a waste including contaminated soil is not included in the list above and is not known or suspected of containing elemental or reduced forms of S, then these *Guidelines* do not apply to that waste and thus no testing for S is required when characterizing the waste/soil.

5.1 Classification of Sulphur Waste

Despite the *TDGR* classification described in section 2 for solid or molten S and spent iron sponge, S-waste including S-contaminated soils is not classified as hazardous waste in Alberta regardless of the S content, provided that:

- (a) the management of the S-waste and S-containing soil is in compliance with these *Guidelines*; and
- (b) S is the only contaminant of concern (*Alberta User Guide for Waste Managers*, 1995, Part 1A, pg 21), or
- (c) the S-waste is not liable to spontaneous combustion when it is being handled or disposed of.

These conditions imply that: (1) the S-waste is conditioned with alkaline products prior

to and/or during disposal as described in section 4.1; (2) the presence of possible contaminants such as hydrocarbons, other organics, salts, heavy metals, or naturally occurring radioactive material (NORM), common in some S-wastes, is not at hazardous levels; and (3) potential pyrophoric S-waste is kept moist at all times and/or bagged/contained to prevent exposure to air and flammability upon removal from the absorption tower and subsequent handling as a waste.

The presence of substances other than S may trigger, depending on the concentration, the presence of hazardous characteristics and/or the need to adopt additional precautions to ensure the safe and environmentally management of the S-waste or S-containing soils.

5.2 Neutralization of Sulphur Waste (or Sulphur Containing Soil)

When managing S-waste including S-containing soil (excavated or *in-situ*) it is important to know when and how much alkaline material needs to be added to the S-waste or the S-containing soil in order to properly neutralize the S present. To determine the correct amounts information from the following questions should be used together with what is described in section 4.1:

- (a) What is the concentration of S in the waste or soil? Does it exceed 0.05% or 500 milligrams per kilogram?
- (b) Does the 500 mg/kg referred in (a) represent S in a combined total concentration of elemental (S°) and reduced (S²-) forms, only?
- (c) Do we know the acid neutralizing capacity (ANC) of the S-waste or S-containing soil to accurately calculate the amount and/or thickness layers, as applicable, of the alkaline product needed?
- (d) What type of waste are we dealing with? Is it homogeneous soil or waste constituted by heterogeneous industrial equipment or debris with visible S as incrustations or scaling?
- (e) Does the waste result from specific chemical processes? Is it known for its S content (elemental or in reduced form)?

In S-containing soil, the S present is typically elemental S, but in some S-wastes such as spent sweetening agents or used catalysts it might be present as a mixture of free S, sulphides, etc. Wastes with S as a sulphate are not subject to these *Guidelines* as the S cannot be further oxidized to produce an acid.

When S is present in wastes or soils it is important to know, in addition to the concentration of S and any other contaminants present, what is the calcium carbonate equivalent (or the ANC) of that waste or soil. Some wastes and soils have a significant alkaline buffer capacity that may be taken into account when calculating the actual quantity of alkaline material needed in each particular case. This knowledge is particularly important when dealing with large quantities of homogeneous wastes/soils with low S content.

5.3 <u>Beneficial Use of Sulphur Waste</u>

The person responsible for S-waste intended for beneficial use must characterize the waste, process it as required into a product, and develop a MSDS for the product derived from the S-waste which identifies at a minimum:

- the product, origin, and intended use,
- physical/chemical/biological properties,
- · precautions and procedures for use,
- potential adverse health and environmental impacts, and
- disposal methods if it becomes a waste.

The MSDS must accompany the S-waste from producer to user to ensure that workers occupational health and safety and the environment are protected.

6 Landfill Disposal of Sulphur Waste

The ultimate objective when disposing S-waste with alkaline material is to prevent S oxidation, neutralize the sulphuric acid eventually formed, prevent migration of acidic leachate from the landfill cell/trench, and ensure that the landfill operator has adopted proper cell/trench landfill designs that optimize landfill space, minimize liability, and protect the environment.

These *Guidelines* address separately the landfill disposal of small and large quantities of S-waste. This approach has been adopted based on operational, economic and environmental reasons. Overall, the most suitable disposal method should be decided on a case-by-case basis depending on the assessment without limitation of the following factors:

- type and quantity of S-waste,
- · access to recovery technologies,
- availability of alkaline products, and
- landfill space.

Regardless of the disposal method, in all cases when handling S-waste at landfills, emergency S-fire fighting equipment must be available and S-dust control measures implemented as required.

The main objective in landfill disposal of S-waste is to ensure that the cell/trench design and operational procedures prevent the formation of acidic leachate.

Approved Class I or II landfills may accept S-waste for disposal along with the appropriate alkaline product for neutralization of the waste (by mixing or encapsulation) as described in these *Guidelines* provided that that:

- (a) appropriate approvals/authorizations as per section 3 have been obtained by the appropriate regulatory authority; and
- (b) the landfill operations plan reflects applicable handling and disposal practices consistent with the approval and/or these *Guidelines*,

S-waste with non-recoverable S, such as S-containing soil, non-usable equipment with S incrustations or scaling, spent sweetening agents, or used catalysts should be conditioned and disposed of with alkaline products as described in this section of the *Guidelines*. When contaminants other than S are present, they have to be characterized and taken onto account for waste classification, facility design, recovery, treatment, or disposal options. Common contaminants include heavy metals, hydrocarbons, glycols, amines, other organics, or naturally occurring radioactive material.

When disposing of S-containing soil, the ANC of the S-containing soil may be taken into account when calculating the quantities and/or layer thickness of the alkaline product required. However, in no case should the layer of alkaline material be reduced from the values indicated in section 6.1 and 6.2 when the total S content in the soil or waste exceeds 4%.

6.1 Small Quantities of Sulphur Waste

When disposing of small quantities of S-waste at approved Class I or Class II landfills, the person responsible for the S-waste and the person responsible for the landfill receiving the S-waste must jointly ensure that the S-waste is mixed stoichiometrically with alkaline product prior to or upon disposal. This is critical when the small quantity of S-waste is disposed of into a cell/trench that has not been specifically designed to receive industrial waste or S-waste only.

Exceptions to mixing may apply when the small quantities of S-waste is

- pyrophoric S-waste such as spent iron sponge being disposed of at Class I landfills; or
- industrial equipment such as containers, vessels, heat exchangers, piping, or similar units not suitable for mixing with alkaline products; or
- disposed of into a cell or trench dedicated to S-wastes only.

In these cases, the S-waste must be disposed of as per the encapsulation *alternating method* described in 6.2.2. Persons responsible for pyrophoric S-waste should take special precautions when handling, transporting, storing and disposing of this waste by keeping it moist to prevent the fire hazard. Pyrophoric waste can not be disposed of into approved Class II landfills unless the waste is previously treated to a non-hazardous condition.

Co-disposal of S-waste with municipal solid waste is not an acceptable waste management practice.

Certain S-waste spent slurries or sludges from gas sweetening processes must be dewatered to a solid condition prior to landfill disposal of the solids. The liquid phase has to be further treated and/or disposed of at approved facilities.

The following applies to landfill disposal of small quantities of solid S-waste:

- (a) an area should be designated for the disposal of S-waste within a landfill cell/trench where incompatible wastes (municipal solid organic wastes and other wastes prone to generate acidic leachates) must not be co-disposed of with the S-waste.
- (b) the designated area shall be at least 1.5 m above the water table;

- (c) the bottom and sides of the designated area should be lined with a 0.30 m thick layer of finely ground alkaline product applied in consecutive compacted lifts 0.10-0.15 m (4-5 inches) thick;
- (d) at the generating site or immediately upon arrival at the landfill, the S-waste should be mixed with alkaline product prior to or after placement in the cell/trench at the ratios described in section 4.1. (Note the exceptions mentioned above for pyrophoric S-waste, industrial heterogeneous equipment, or multi-loads of small quantities of S-waste going to the same dedicated cell/trench described in section 6.2.2.)
- (e) after mixing and/or layering, the S-waste should be immediately covered with a uniform layer of alkaline material in an amount and thickness equal to 10-15 % of the amount used to line the cell; and
- (f) an intermediate or final cover, as applicable, shall be applied over the S-waste plus alkaline material to prevent water percolation.

Limestone, lime or other alkaline products used as neutralizing agents in landfills should be no coarser than the commercially available product known as "3/8th minus". A laboratory investigation which involved leaching a solution of sulphuric acid through columns of this limestone product indicated a considerable margin of safety is provided as long as a significant content of fine particles is present. Removing the particles which pass a 60 mesh sieve significantly increased the percolation rate and jeopardized pH control. The limestone grain size has to be balanced with site stability, erosion and dust formation.

Alkaline materials, other than those identified in section 4.2, have to be assessed on a case by case basis with respect to their ANC (expressed as calcium carbonate equivalent) and other constituents/contaminants that might be present.

The objective in lining the disposal cell with alkaline material is to provide additional safety against the formation of acidic leachate. When disposing of small quantities of S-waste into cells/trenches that are not dedicated to S-wastes only, a layer of limestone/lime about 0.3 m thick should provide such a margin of safety. Between active disposal periods, an intermediate cover, preferably an alkaline product or buffer should be placed on top of the S-waste to minimize dust, erosion and leachate.

6.2 Large Quantities of Sulphur Waste

The landfill disposal of large quantities of S-waste discussed here follows methods that are not based on the stoichiometry of the reaction referred to in section 4.1. Instead, the S-waste is encapsulated within layers of suitable alkaline material.

Mixing large quantities of S-waste with alkaline material at the rates indicated in section 4.1 would multiply the waste volume by a factor of at least 3 or 4 depending on the alkaline material used. This is neither economical nor environmentally sound since both landfill space and alkaline materials are often scarce. Consequently, the encapsulation of a large quantity of S-waste within a layer of suitable alkaline material acting as a buffer barrier is preferred over the stoichiometric mixing when disposing of large quantities of S-waste into a dedicated landfill cell/trench.

When disposing of S-waste by encapsulation into a dedicated landfill cell/trench no mixing of the S-waste with alkaline material is required. Consequently, the ratios indicated in section 4.1 do not apply.

Those large quantities can occur as one time event or result from multiple loads of small or large quantites of S-waste produced over a short period of time that should not exceed a maximum of two continuous calendar months. In summary, a homogeneous large quanty of S-waste or a large quantity constitued by the accumulation of multiple alternating layers of small or large quantities of S-waste and alkaline material or intermediate cover must not be mixed with additional alkaline material but rather encapsulated as described in 6.2.1 and 6.2.2.

6.2.1 Encapsulating Large Quantities of S-Waste

Basically, large quantities of S-waste resulting from train derailments, off-spec S, contaminated S, and S-containing soil with unrecoverable S should be preferably disposed of into dedicated cells/trenches at approved Class I or Class II landfills that respect the following design and operational requirements:

- (a) a location within the industrial disposal area or a dedicated cell/trench (it is assumed that the overall site is hydrogeologically suitable) shall be designated for the disposal of large quantities of S-waste;
- (b) the S-waste cell/trench shall be large enough to allow for expansion as required, but it should minimize
 - (i) the active S disposal area, and
 - (ii) airborne particulate matter by adopting dust control and synthetic/alkaline product intermediate covers;
- (c) upon delivery to the site, the S-waste shall be immediately deposited into the previously prepared designated area or cell for disposal;
- (d) within the designated area or cell/trench, the S-waste should be totally encapsulated (i.e. the base, sides and top) with alkaline material to:
 - (i) neutralize potential acidic leachate;
 - (ii) minimize waste volume; and
 - (iii) facilitate mining of the S-waste if that becomes a future option;
- (e) the bottom and sides of the cell/trench should be lined with a 0.60 m thick layer of fine-grained alkaline product (for example, 3/8^{ths} minus limestone, lime, or equivalent alkaline product) applied in consecutive compacted lifts 0.10-0.15 m thick;
- (f) the S-waste should be:
 - (i) delivered to the designated area or dedicated cell in bulk with no

mixing of the S-waste with alkaline product,

- (ii) placed directly on the bed of alkaline product,
- (iii) compacted as needed to minimize voids;
- (iv) developed until the final design height is reached, and
- (v) covered in the following order with:
 - A. a 0.15 m layer of alkaline product;
 - B. a low permeability cap sloped to avoid percolation of infiltration water;
 - C. a sloped drainage layer of coarse material; and
 - D. a final cover of sufficient thickness to avoids erosion, water accumulation, and support vegetation;
- (g) any leachate, passing through the S-waste should be collected and controlled in the leachate collection system;
- (h) the operation of a cell dedicated to S-waste should not allow for:
 - (i) oxidation of S present in the waste;
 - (ii) water accumulation on and/or infiltration into the S-waste during operation or post-closure to minimize aerobic/anaerobic activity;
 - (iii) co-disposal of the S-waste with municipal solid waste;
 - (iv) leachate recirculation to reduce formation of acidic leachate, mobilization of heavy metals, and waste destabilization; and
 - (v) capture of landfill gas;

Regardless of the degree of the landfill cell/trench design (bottom liners, leachate collection systems, etc...) the disposal of large quantities of S-waste at approved landfills with dedicated S-cells should respect the encapsulation process described in these *Guidelines*.

6.2.2 The Alternating Method

The encapsulation method can be modified as necessary to accommodate the disposal of multiple small or large loads of similar S-wastes received and disposed into the same dedicated landfill cell/trench provided that:

- (a) the individual shipments are received within a limited period that should not exceed two continuous calendar months; and
- (b) the multiple loads of S-waste are disposed into a dedicated landfill cell/trench in sequencial alternating layers of alkaline material or intermediate cover and S-waste.

In the *alternating method*, the layer of alkaline product functions simultaneously as buffer and as intermediate cover. This method is particularly suitable when small quantities of S-waste are produced over a limited time, the potential for recovery of the S-waste is low, and/or it is difficult to obtain alkaline products. Most importantly, there is

no need to mix the S-waste with alkaline products.

The intermediate cover may take the form of temporary or removable tarps, plastic liners, synthetic geotextiles, clay or other suitable material that minimize airborne S particulate matter and preclude percolation of water through the S-waste.

6.3 Monitoring

The presence of large quantities of S-waste in dedicated landfills cells or trenches may trigger additional monitoring to assess performance of the cell or trench and the landfill in containing these wastes. The extent of these monitoring provisions, if not part of the existing approval, is described next and must be added as part of an amendment of the landfill approval.

For further guidance on comprehensive landfill monitoring consult the *Standards for Landfills in Alberta* at http://environment.alberta.ca/02956.html. The monitoring provisions, triggered by the presence of large quantities of S-waste, include, without limitation the following:

- (a) measuring the quantity, type, and chemistry of the S-waste received and disposed of;
- (b) measuring the quantity, type, and chemistry of the alkaline product admixed and/or used as encapsulating buffer;
- (c) recording and mapping the exact disposal location of the S-waste;
- (d) recording the design, construction, operation, and reclamation of the S-waste cell/trench;
- (e) the leachate from each cell containing S-waste should be tested biannually for pH, sulphates, and heavy metals including vanadium; (3)
- (f) water accumulation and infiltration within areas containing S-waste;
- (g) controlling S dust, as needed; and
- (h) additional groundwater well(s) installed up-gradient and immediately downgradient, adjacent to the S-waste cell/trench, as part of the landfill groundwater monitoring system.

This landfill monitoring information should be collected during operation, closure and post-closure periods. Record keeping and reporting should be maintained as per the *WCR* or specific approval requirements.

7 Remediation of Sulphur Containing Soil

Remediation and land application applies only to S-containing soil. Contaminated S, unrecoverable S, and off-specification S may be candidates to land application provided that these materials do not contain constituents detrimental to the soil systems or cause odours and are in compliance with section 7.2.

Upon removal of the most free and visible S from S-block storage areas, the concentration of total S left in the soil should not exceed 4% [elemental S plus sulphate (SO₄)]. This soil with low S content may be left in place provided that *in situ* land surface remediation with limestone or lime is done as described in section 7.1. Though suitable alternative alkaline products may be used, limestone is preferred to other products because of its longer term ANC. When residual S in the base soil is less than 0.05% (or 500 parts per million on a weight basis) no liming is required.

The materials removed during S storage block area clean-up activities, including excavated contaminated soil, base aggregates and/or liners, contaminated S, unrecoverable S, and off-specification S, must be sent to a S recovery facility or managed as described in section 6 or 7.2 of these *Guidelines*. Some of these materials may be suitable for land application to S-deficient soils provided that S recovery is not feasible, do not contain constituents that could be detrimental to the soil system, and do not create odours. On-site dilution of contaminated material to reduce S content to below 4% total S is not allowed. Soils containing more than 4% total S are not suitable for *in situ* liming and should be removed from the contaminated site for S-recovery or disposal.

When transfering S-waste or alkaline products derived from waste to a third party for land application, the person responsible (generator/producer/owner) for the S-waste and/or alkaline product shall develop applicable MSDS sheets and provide a copy to the receiving party.

S materials should not be applied to soils with an initial pH less than 6.5. To ensure effective oxidation of the S within the top layer of soil and crop benefit, S particle size should not exceed 2 mm (0.08 in).

7.1 In Situ Land Remediation

In situ land remediation (1) refers to the treatment with alkaline product of

- (a) the top layer of S-containing soil that remains on former S storage block areas after removal of all the S, and S-wastes; or
- (b) S-contaminated soil due to dusting in the vicinity of S-block storage areas;or
- (c) the land area where an accidental spill of S has occurred;

and the total residual concentration of S is between 0.05% elemental S and 4% total S (or 500 mg elemental S/kg and 40 000 mg total S/kg, respectively).

This means that most free and visible S, S-containing soil/material, or S-waste with an excess of 4% total S have been removed from the former S-storage block or otherwise S-affected areas prior to *in situ* liming. Then, alkaline product must be applied to the affected land in accordance with the following:

- (d) the application rates reflect the chemical reactions depicted in section 4 of these Guidelines;
- (e) the magnesium carbonate content of the limestone does not exceed 2% by weight;
- (f) the alkaline product is finely ground so that 90% passes a 60 mesh sieve; and
- (g) airborne particulate matter is minimized.

In situ land treatment with limestone is not required when the residual elemental S soil content is less than 0.05% (500 mg S/kg) and the soil pH is higher than 6.5 (measured in 0.01 M CaCl₂). A balance has to be reached in each case in terms of the soil S-content versus limestone requirements as limestone generally decreases the availability of sulphates for plants (2).

7.2 Land Application

Land application (3) of suitable S-waste to agricultural soils refers to the occasional application of S to soils that are S-deficient, high in carbonates, or required to grow specific crops. When S is finely ground and mixed with soils with high oxidizing capacity it is usually just as effective as alternative SO_4 sources (4). Time of application of S-waste is also critical as it should be worked into the soil as far ahead of planting as possible.

Prior to or immediately after the application of S-waste to land, ground limestone may have to be spread over the S treated area for pH control. Both, the S-waste and the limestone, have to be incorporated homogeneously into the surface 15 cm (6 in) of the soil using suitable tillage equipment. The following should be respected when applying S-waste to soils:

- (a) the application rate of S to the land should be based on a fertilizer recommendation prepared by a Professional Agrologist and should not exceed a maximum rate of 250 kilograms elemental S per hectare (or about 223 pounds per acre);
- (b) S particle size should not exceed 2 mm (0.08 in);
- (c) no S application should take place on soils that
 - (i) have a pH of less than 6.5,
 - (ii) are saturated with water,
 - (iii) is covered with ice or snow,
 - (iv) is frozen, or

- (v) at any time where conditions preclude effective application and incorporation;
- (d) the targeted agricultural land should not be used for S application more than once every 3 or 4-year cycle, or as determined by a fertilizer recommendation:
- (e) additional application of S to the same area should not occur until the previously applied S has been oxidized;
- (f) when needed, the application of limestone should
 - (i) accompany each application of S-waste, and
 - (ii) comply with section 7.1(d) (f);
- (g) between consecutive applications of S, the land should be sown to a grass mixture or cropped (i.e., it must support vegetation); and
- (h) land management must ensure the wastes applied are retained on the top soil where they are spread.

A Professional Agrologist may recommend application rates for sulphur and/or limestone that may differ from those indicated in section 4 and 7.

When S-waste or alkaline product derived from waste are to be used, detailed chemistry including the soil oxidizing capacity, the alkaline product ANC (often expressed as calcium carbonate equivalent), and the concentration of non-oxidized forms of S (elemental and sulphides) is required. The application rates to land for S or lime/limestone indicated in sections 4.1 or 7.2 may vary subject to the assessment of a Professional Agrologist.

7.3 Soil and Water Monitoring

Soil, surface water, and when needed, groundwater monitoring of the land area receiving S and alkaline buffer products should be conducted to:

- (a) assess the impact of these substances on the targeted land;
- (b) confirm that S oxidation has been achieved; and
- (c) assess soil and water pH, especially when the land receives more than one application of S.

Documentation to be collected and submitted must address the elements identified in Sections 3 to 7 of these *Guidelines*, and should include data which demonstrate effective *in situ* remediation in the case of cleaning up former S block storage areas or spills, or effective use of S as a soil fertilizer in the case of application of suitable S-waste to S-deficient soils.

7.3.1. Soil Monitoring

Representative soil samples shall be taken and tested from at least four locations within each land treated area (1) prior to land application, (2) at least once within two months after land treatment, and (3) quarterly thereafter until soil pH stabilizes within 6.5 and the background value. In doing so, the following factors should be taken into account:

- (a) at each location the soil samples shall be representative of the soil horizons at 0 to 0.15 and 0.15 to 0.30 m depths; and
- (b) the soil analyses should include at a minimum
 - (i) pH (in 0.01 M CaCl₂),
 - (ii) elemental S,
 - (iii) total S (elemental and sulphate)
 - (iv) ANC (often expressed as CaCO₃ equivalent), and
 - (v) electrical conductivity.

Soils with low pH (i.e. with a pH below 6.5) would trigger further testing including heavy metals. The results obtained should be compared with similar data obtained from adjacent unaffected soil locations. If needed, soil samples should also be collected from the 0.30 to 0.45, 0.45 to 0.60, 0.60 to 0.90, 0.90 to 1.20, 1.20 to 1.50 m depths and every 0.50 m thereafter throughout the depth of contamination to assess further impact and tested for the parameters in 7.3.1 (b).

7.3.2. Groundwater Monitoring

Groundwater monitoring hydraulically up-gradient, immediately down-gradient of the S-affected land, and within the land application area is required on an annual basis when acidification of the subsoil above the water table has been detected. This is more likely to occur upon multiple applications of S to the same area. Groundwater monitoring, if needed, should take into account the following:

- (a) the location of acidification (with one sample per each of the acidified sampling area with a maximum of 2500 square metres);
- (b) areal and depth extent of the acidification and/or contamination;
- (c) soil testing results and trends;
- (d) depth of local water table;
- (e) be conducted for as long as soil acidification persists; and
- (f) sample parameters to be tested include pH, SO₄, vanadium and other heavy metals.

8 Test Methods, Record Keeping, and Reporting

Often S-wastes and S-containing soils are rather heterogeneous materials. Thus, the collection and preparation of homogeneous and representative samples for analytical testing is a significant challenge. This is well illustrated with elemental S for which current test methods require a 0.2 milligram size sample and/or different solvents. Another recurrent issue is inconsistency of results due to the different methodologies used when testing elemental S, total S, sulphates, and other S-soil related parameters referred to in these *Guidelines*.

There is a need for further identification and standardization of reliable and cost effective tests methods for testing S and S-soil related parameters. In the interim, and to minimize sample variability and increase consistency, it is recommended that large enough samples be obtained and homogenized for representativeness prior to collection of the required aliquot for testing using:

- (a) standard test methods when available,
- (b) the test methods identified in Table 1 of AENV draft *Directive for Monitoring* the *Impact of Sulphur Dust on Soils* available on-line at http://environment.gov.ab.ca/info/library/8368.pdf; or
- (c) alternative test methods adopted by a laboratory accredited pursuant to ISO 17025, as amended, unless otherwise authorized in writing by the regulatory agency.

The test methods recommended for better established water and wastewater (leachate), soil and solid waste analysis mentioned in these *Guidelines* and in AENV approvals are also identified in Appendix 1.

All information collected in compliance with the monitoring requirements of these *Guidelines* (e.g. in sections 6.3 and 7.3) shall be recorded, kept by the person responsible for the activity, and reported as required in the approval to operate the facility, if one is required, or upon written request of the Director. In addition, the type and quantity of S-waste produced and disposed of should be recorded and reported in the facility's *annual summary of waste management data* to the regulatory agency, if required by the applicable approval, or recorded in the landfill operational plan and kept on site.

Any environmental releases involving contaminated elemental S not addressed in the facility approval to operate shall be reported by the person responsible immediately upon discovery. Reports shall be made by phoning the toll free 24-hour Alberta Environment hotline at 1-800-222-6514. More information on reporting spills/releases is available at http://environment.alberta.ca/01521.html.

REFERENCES

- 1. Alberta Environment, Standards and Approvals Division, *Guidelines for the Disposal of Sulphur Containing Solid Waste*, 1983.
- 2. Rechcigl, Jack E., editor, *Soil Amendments and Environmental Quality*, Lewis Publishers, 1995.
- 3. Alberta Environment, Chemicals Assessment and Management Division, *Guidelines for the Remediation and Disposal of Sulphur Contaminated Solid Wastes*, 1996.
- 4. Tisdale, Samuel L., Nelson, Werner L., and Beaton, James D., *Soil Fertility and Fertilizers*, Macmillan Publishing Co., 4th Edition, 1985.
- 5. Alberta Environment, *The Elemental Sulphur Management Framework for the Industrial Heartland*, undated.
- 6. Alberta Environment, Air, Land, and Strategic Policy Branch, *Directive for Monitoring the Impact of Sulphur Deposition on Soils*, 2011.
- 7. U.S. Department of Energy, Characterization *and Disposal of By-Product Elemental Sulphur*, Prepared by the Oak Ridge National Laboratory, 1986.
- 8. Chapin, D., Jarrett, F., Johnson, J., and Worah, V., Should I Make Sulfur or Reinject the Acid Gas, Presented at GPA Rocky Mountain Regional Mtg., Greenwood Village, CO, USA, September 21, 2000.
- 9. Energy Resources Conservation Board *ID 2001-3, Sulphur Recovery Guidelines for the Province of Alberta.*
- Sourisseau, K., Energy Balance and Green House Gas Impacts of a Large Scale Acid Gas Injection Scheme, Presented at Sulphur 2000, San Francisco, CA, USA, October 29-November 1, 2000.
- 11. Ghosh, S. N., *Advances in Cement Technology: Chemistry, Manufacture, and Testing*, 2002, 2nd Edition, Tech Books International, New Delhi, India.
- 12. Paul Davis, ASRL, Center for Applied Catalysis and Industrial Sulfur Chemistry, Department of Chemistry The University of Calgary, *Perspectives on Sulphur Management*, Presented at the Topsoe Catalysis Forum 2007, Hornbaek, Denmark.
- 13. F.A. Lopez et al, Dept. of Primary Metallurgy and Materials Recycling. National Centre for Metallurgical Research, CENIM (CSIC). *Disposal of Elemental Mercury via Sulphur Reactions by Milling*, 1 st International Conference on "Hazardous Waste Management", 2008, Crete, Greece
- 14. United States Patent 7311468, Process for the Disposal of Sulfur.
- 15. Alberta Environment, Alberta User Guide for Waste Managers, 1995
- 16. Environment Canada. 1988. Interim Compilation of Test Methods Under the TDGR, VI.2 Division 4.2: Spontaneously Combustible Substances. CCREM Working Group on TDG Hazardous Wastes. pp. 141-145.

APPENDIX 1: RECOMMENDED TEST METHODS

1. For S and S-Soil or S-Waste Related Parameters

(a) the methods identified in Table 1 of AENV *Directive for Monitoring the Impact of Sulphur Dust on Soils* at http://environment.gov.ab.ca/info/library/8368.pdf.

2. For wastewater, runoff, and groundwater

- (a) the Standard Methods for the Examination of Water and Wastewater, American Public Health Association, American Water Works Association, and the Water Environment Federation, as amended;
- (b) the *Methods Manual for Chemical Analysis of Water and Wastes*, Alberta Innovates, Vegreville, Alberta, 1996, as amended;
- (c) the *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods,* USEPA, SW-846; September 1986, as amended;

3. For soil samples

- (a) Soil Sampling and Methods of Analysis, Lewis Publishers, 1993, as amended;
- (b) the Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, USEPA, SW-846; September 1986, as amended;
- (c) the Soil Quality Criteria Relative to Disturbance and Reclamation, Alberta Agriculture, March 1987, as amended;
- (d) the Guidance Manual on Sampling, Analysis and Data Management for Contaminated Sites Volume I: Main Report, CCME EPCNCS62E, 1993, as amended:
- the Guidance Manual on Sampling, Analysis and Data Management for Contaminated Sites – Volume II: Analytical Method Summaries, CCME EPC-NCS66E, as amended;

4. For waste

- (a) the *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, USEPA, SW-846, Revision 6, 2007 available on-line at http://www.epa.gov/epawaste/hazard/testmethods/sw846/online/index.htm;
- (b) the *Methods Manual for Chemical Analysis of Water and Wastes*, Alberta Environmental Centre, Vegreville, Alberta, 1996, AECV96-M1 as amended; or
- (c) the *Toxicity Characteristic Leaching Procedure (TCLP)* USEPA Regulation 40 CFR261, Appendix II, Method No. 1311, as amended; or
- (d) the Standard Methods for the Examination of Water and Wastewater, American Public Health Association, American Water Works Association, and the Water Environment Federation, as amended; or
- (e) the Alberta User Guide for Waste Managers, AENV,1995, as amended;
- (f) with respect to coal sampling and analytical methods, the applicable requirements in the most recent version of ASTM, as amended.

APPENDIX 2: FREQUENTLY ASKED QUESTIONS

1. When do these Guidelines apply to me?

When you are the person responsible for the generation and/or management of S-waste including excavated S-contaminated soils, the *in-situ* remediation of S-contaminated land, and/or the reclamation of S-storage block base pads and use land-based technologies such as landfills or land application for S-waste management.

2. Does my EPEA landfill approval require an amendment if I want to accept S-waste including off-spec S or S-containing soil for disposal?

An EPEA approval amendment is not required if S-waste disposal related provisions are clearly identified in the landfill approval. The landfill approval should

- (a) contain specific S disposal provisions; or
- (b) specifically require S disposal procedures be part of the operations plan; or
- (c) make reference to the 1983 "Guideline for the Disposal of Sulphur Containing Solid Wastes" as amended, or
- (d) make reference to these *Guidelines*.

If the above are not met, the person responsible must contact AENV regional office, prior to acceptance of the S waste, to determine if an approval amendment or site specific authorization is required.

In any case, the operator of an approved landfill should document the disposal procedures applicable to any particular waste (including S-waste) received at the site that requires special handling procedures and those procedures should be documented in the facility operational plan kept at the site.

3. Can a registered Class II landfill accept large quantities or oilfield S-waste for disposal?

No. If the S-waste is an oilfield waste, ERCB *ID 2000-4* takes precedence. ERCB *ID 2000-4* prohibits oilfield wastes other than demolition debris, garbage, and scrap metal from accessing *EPEA* registered Class II landfills. However, large quantities of S-waste that is not an oilfield waste may access Class II registered landfills provided the registration holder has previously obtained the written authorization of the Director and the activity is documented in the landfill's operational plan.

4. Can I dispose of S-waste, off-spec S or contaminated S at my landfill for possible future mining of S?

A landfill is not a "sulphur storage facility" as defined in the *ADR*. Hence, the storage of S at a landfill can only be accommodated under an approval for a S-storage facility (or an amendment of the current approval). The *ADR* and *IL 84-11* define the production, processing, and storage of S as activities that require EPEA and/or OGCA approvals.

However, the disposal of large quantities of S-waste by encapsulation with limestone, lime or suitable alternative alkaline product at approved landfills is acceptable provided that it is conducted in compliance with section 6.2 of these *Guidelines* and the activity is addressed in:

- (a) the existing approval for the landfill, or
- (b) an amendment of the current approval.

Regardless, any landfill should be designed and operated in anticipation of foreseeable wastes and activities planned for the facility and for what may happen later when reclaiming these sites. Among other, landfill reclamation activities may include landfill gas collection and mining of specific wastes.

5. If my landfill approval references the 1983 guideline, as amended, should I follow these Guidelines?

Yes, you should follow these *Guidelines* because they amend and replace the *Guidelines for the Disposal of Sulphur Containing Solid Waste* (1983) as well as the *Guidelines for the Remediation and Disposal of Sulphur Contaminated Wastes* (1996), published by Alberta Environment effective September 12, 2011.

6. Can I store S at my approved landfill?

No, unless an *EPEA* or an *OGCA* approval for a S storage facility has been issued by AENV or the ERCB, as applicable. A landfill is not a "sulphur storage facility" as defined in the *ADR* and the ERCB *IL* 84-11.

7. Can a S-waste dedicated landfill cell or trench accept other wastes?

Yes, under well defined conditions and subject to case-by-case assessment, wastes other than S-waste are suitable for treating other wastes being simultaneously treated in the process and eventually be disposed in the same cell/trench. Examples include alkaline and elemental mercury (Hg°) wastes. Cases with alkaline wastes are profusely illustrated in these *Guidelines*. As for Hg° waste, treatment options have to be assessed individually. One acceptable method is the treatment by the generator of the Hg° waste by mixing and reacting the Hg° waste with S° followed by encapsulation with alkaline material. The S° needed could come from suitable S-waste that otherwise would have to be disposed of as such. In any case, treatment of Hg° waste with S° has to be properly designed and evaluated to ensure its technical, economic and environmental feasibility. (Example 3 in Appendix 3)

8. Can I co-dispose of S-waste with MSW at my landfill?

No. S-waste should never be mixed and/or co-disposed with MSW at any landfill. However, small quantities of S-waste may be disposed in a MSW landfill cell/trench provided that the S-waste is layered, confined, and physically separated from the MSW by appropriate barriers of alkaline product and/or other suitable waste. Alternatively, small quantities of S-waste or S-containing soil, properly mixed or layered with intermediate alkaline material may be placed preferably at the bottom of the trench or within a designated part of the trench and then totally encapsulated with buffer alkaline material as described in section 6. In this case, the alkaline material also functions as intermediate cover.

9 Do debris with minor dusting of S on the surface, but no visible solid or scaled S, require the addition of alkaline material when landfilled?

Assuming that the S dusting was not from direct exposure to S manufacturing, processing, or

recovery operations and was caused presumably by the deposits of air borne S particulate matter from S handling or storage, then the debris with minor dusting is not considered an S-waste. However, this debris would not be considered an inert waste and should not be disposed of in a Class III landfill. Check also the criteria in section 5.

10. Does a landfill operator have to develop specific landfill procedures including S-waste management protocols when receiving S-waste?

Yes. The person responsible for the operation of a landfill must include in the landfill operations plan all the procedures and protocols required to properly handle S-waste received at the site.

11. Does a landfill with an engineered liner and leachate collection and removal systems still require the co-disposal or encapsulation of the S-waste with suitable alkaline materials?

Yes. The addition of alkaline products as a buffer or neutralizing agent to S-wastes – either by mixing or encapsulation – constitutes a mandatory precautionary measure to account for potential operational mismanagement of the landfill, the neutralization of potential acid leachate, liner protection, and the landfill post-closure period when the maintenance, leachate control and monitoring systems are no longer in place.

12. Can I receive spent iron sponge (i.e. a pyrophoric waste, TDGR class 4.2) for disposal at my Class I landfill?

Yes, provided that the spent iron sponge is conditioned so that it does not ignite under the conditions of disposal [s 13(2)(c), WCR]. This is done by keeping the waste wet and contained upon removal from the absorption tower up to disposal with lime or limestone as indicated in section 6.1.

Iron sponge consists of wood chips impregnated with iron oxide (Fe₂O₃) and it is used to remove hydrogen sulphide and other S compounds from slightly sour natural gas. During this sweetening process the following reaction occur:

(a) Ferric oxide (impregnating wood chips) reacts with H₂S to sweeten slightly sour natural gas producing water and ferric sulfide:

$$2Fe_2O_3 + 6H_2S \rightarrow 2Fe_2S_3 + 6H_2O$$
 (1)

The spent iron sponge is a hazardous pyrophoric waste, class 4.2, that can be regenerated a number of times but eventually has to be disposed of.

(b) Regeneration (or **treatment to a non-hazardous condition**) is achieved by allowing the ferric sulfide to react with air:

$$2Fe_2S_3 + 3O_2 \rightarrow 2Fe_2O_3 + 6S + \Delta H$$
 (2)

This is a spontaneous exothermic reaction controlled by keeping the iron sponge wet to prevent spontaneous combustion. This reaction may take a few days and is complete when the black spent iron sponge turns red.

(c) In the presence of enough heat, the S is burned producing sulphur dioxide:

$$2S + 2O_2 \rightarrow 2SO_2 \tag{3}$$

Of course, in the absence of air, reactions (2) and (3) do not occur and the waste

must be co-disposed with limestone/lime at approved Class I landfills as described in section 4.1 of the *Guidelines*.

13. Can I receive spent iron sponge at my approved Class II landfill?

Not as produced since spent iron sponge is a hazardous pyrophoric waste. See FAQ 12.

However, this waste can be easily treated by the generator as illustrated by the process described in FAQ 12. To confirm treatment performance, representative samples have to pass the test for spontaneously combustible substances (15) and (16)

14. May these Guidelines be used as guidance when preparing an application for an approval to store S by entombment?

Yes, as applicable. In particular, sections 6.2 to 6.3 of these *Guidelines* may assist in the development of the application for an approval, particularly with respect to the design and monitoring of the S-storage cell or trench.

15. Where can I find information regarding the approvals required for the production, processing, and storage of S?

ERCB Information Letter 84-11 and the ADR pursuant to OGCA/OSCA or EPEA, respectively provide information on the approvals required for these activities.

16. How do I measure the pH of soils with sulphur?

The soil pH is measured in a 1:2 (w/v basis) equilibrated slurry of soil to 0.01 mole solution of $CaCl_2$ or by using laboratories accredited pursuant to ISO/IEC 17025 (for more information on test methods see Alberta Environment's 2009 *Directive Soil Monitoring* at http://environment.gov.ab.ca/info/library/8159.pdf.

17. What is the level that renders soil containing sulphur, as sulphate, contaminated soil? Is a soil with 5 000 mg/kg of S (as sulphate) considered contaminated? At what levels do sulphates become a contaminant of concern?

Oxidized S in soils as sulphate (SO_4^{2-}) is not generally considered a soil contaminant and sulphates maximum levels in soils are not regulated in Alberta. Soil with 5 000 mg/kg of S as sulphate is not considered contaminated if the soil pH exceeds 6.5 units. (*Guidelines*, sections 4.2, 7.1 and 7.2).

The total combined concentration of reduced S plus elemental S in soils that triggers remediation or application of suitable alkaline compounds to soils is soil with S in excess of 0.05% or 500 mg/kg on a dry weight basis.

Regarding acceptable levels of soluble sulfate (SO₄²⁻) in soils the following thresholds may be used as a reference:

- Not a concern: below 0.3% or 3,000 mg /kg;
- *Moderate risk*: between 0.3% (3,000 mg/kg) and 0.5% (5,000 mg/kg)
- Moderate to high risk: between 0.5% (5,000 mg/kg) and 0.8% (8,000 mg/kg)
- Unacceptable risk: greater than 0.8% (8,000 mg/kg soils with total soluble sulphate

contents greater than 1.0% (10,000 ppm) generally are not suitable for lime stabilization because of the high risk of sulphate-induced disruption and failure.

More detail on soluble sulphate in soils at http://www.griffinsoil.com/sulfate study.

18. Is an MSDS required for S-waste applied to agricultural land?

Yes. MSDS are required for both "alkaline products" and "S-waste" identified in Sections 4 and 5, respectively, when used as described in sections 6 and 7 of these *Guidelines* (i.e. *in situ* treatment, land application, and disposal of S-waste) or other beneficial uses.

19. What is a fine-grained soil?

Fine-grained soil means soil that has a median grain size less than or equal to seventy-five (75) micrometers, determined in accordance with the *Standard Test Method for Particle-Size Analysis of Soils*, published by the American Society for Testing and Materials, Test Method D422-63, 1998, as amended. Fine-grained soil generally includes clay, silty clay, and sandy clay.

20. Why should dolomitic limestone not be used?

Because the oxidation of limestone with more than 2% magnesium carbonate will generate significant amounts of highly soluble magnesium sulfate that may migrate from the site and adversely affect local soil quality.

21. When do I have to test limestone, lime or alternative alkaline material for the ANC?

Pure grade commercial available lime or limestone should not require routine testing and the specifications of the product should respond to the purity of the material. However, when alternative products are used the ANC should be determined to ensure that the ratios S-waste/alkaline material and the thickness of the required alkaline material are adequate. See section 4.2.

22. What is the oxidizing capacity of a soil?

The oxidizing capacity of a soil reflects its redox potential. It shows the potential of that the soil to add or remove electrons from a particular element or compound added or present in that soil. From measuring the soil redox potential we can estimate whether the soil is aerobic, anaerobic, and whether chemicals such as S or S compounds will be chemically reduced or oxidized.

23. Can alternative alkaline products derived from waste be used in co-disposal or neutralization of S-waste?

Yes. Alkaline products derived from wastes may be used as substitute products to buffer S-waste. However, when used for this purpose, these alternative products must be supported by a case-by-case assessment which must identify the following:

- (a) the ANC (often expressed as calcium carbonate equivalent),
- (b) the moisture content,
- (c) any constituent or contaminants present, and
- (d) an applicable Material Safety Data Sheet

Subject to assessment, candidate wastes may include wood ash, fossil fuel, fly and bottom ash, lime sludges, cement kiln dust, crushed concrete, excess/junk cement, or other alkaline

product derived from waste that are free of soluble ions or hazardous constituents/contaminants.

24. Can I use crushed concrete as an alternative alkaline product to mix with or encapsulate S-waste?

Yes, if the material has a suitable ANC. The use of alkaline products alternative to limestone or lime, discussed in section 4, is acceptable and recommended provided that the person responsible determines the potentially reactive alkaline content of the candidate product. For crushed concrete, the rationale to determine the amount of concrete equivalent to the stoichiometric quantities indicated in Section 4 is illustrated next. The basic reaction when concrete reacts with oxidized S is:

$$3(CaO) \cdot 2(SiO_2) \cdot 4(H_2O)(gel) + 3Ca(OH)_2 + 6SO_4^{2-} \rightarrow 6CaSO_4 + ...$$

Taking an average mass increase of about five times due to the addition of sand and aggregate to Portland cement to produce concrete, the resulting weight ratio concrete/S is about 6.5 (i.e., about 6.5 kg of crushed concrete are needed to potentially neutralize one kilogram of S present in the S-waste or S-contaminated soil). Because concrete shows about half the buffering capacity of pure limestone, the thickness of the bottom and side layers of the crushed concrete should be double the thickness indicated in section 6.2(e) for limestone.

25. What gaseous emissions should be monitored when disposing of large quantities of S-waste?

S-dust and associated particulate matter (PM) should always be controlled at a landfill site and in particular the PM created when handling S-waste. On the other end, the disposal of large quantities of S-waste is not expected to generate significant S gaseous emissions.

Even though the occurrence of fires at S facilities is a rare event, emergency S fire fighting equipment should be always available at landfills handling large quantities of S. S fires are hard to put out and when they occur large quantities of SO₂ are released. Other gas releases are not relevant and the important thing is to put out the fire.

Where can I find information on specific test methods for S when managing S-wastes and remediating S-containing soils?

Information on analytical methods for soil S parameters and S related test methods is available in the AENV draft *Directive for Monitoring the Impact of Sulphur Deposition on Soils*" available at http://environment.gov.ab.ca/info/library/8368.pdf.

Questions on sulphur-soil parameters and test methods identified in this Directive can be directed to

Air, Land and Waste Policy Branch Alberta Environment 10th Floor, Oxbridge Place 9820-106 Street Edmonton, Alberta T5K 2J6 phone: (780) 427-5125

fax: (780) 422-4192

email: AENV.AMD@gov.ab.ca

APPENDIX 3: EXAMPLES

Example 1: Calculation of the Calcium Carbonate Equivalent (CaCO₃) in Cement and Drilling Mud Mixtures

One method of calculating the ANC (expressed as $CaCO_3$ equivalent) in mixtures of cement/drilling mud (CDM) mixtures (or in concrete) is to react a representative sample of the CDM mixture with excess acid and then titrate the excess acid with a strong base. In the case of sulphuric acid and sodium hydroxide the basic reactions involved are:

$$3(CaO) \cdot 2(SiO_2) \cdot 4(H_2O)(gel) + 3Ca(OH_2) + 6 H_2SO_4 \rightarrow 6CaSO_4 + ...$$
 (1)

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$$
 (2)

Once the quantity of acid unused is known it is easy to calculate the weight of the acid neutralizing compounds present in the CDM mixture and from that, the weight of CDM mixture required to neutralize a given weight of S present in the S-waste.

Example 2: Reclamation of a Sulphur Base Pad

This option is advisable when cleaning up S base pad material or S spills. The remaining material or soil should not contain more than 4% total S (or 40 000 mg total S/kg). The affected area should then be treated with alkaline product as outlined in section 7.1 of these *Guidelines*.

Options available to deal with the free S present in the material removed from the S base pad and containing over 4% total S, soil or gravel include:

- further recovery of S by using for instance froth flotation,
- use as fertilizer in S-deficient agricultural soils as outlined in section 7.2, or
- disposed of in an approved landfill or, with the appropriate authorization, buried in a registered landfill as described in section 6.

Example 3: Disposal of Mercury Waste with Sulphur

A simple method of safely disposing of small quantities of mercury waste is by first stabilizing the waste mercury by mixing and encapsulating the waste with sulphur or calcium sulphide. The mercury will react slowly with the sulphur or calcium sulphide to form the extremely insoluble mercury (II) sulphide (HgS) similar to the naturally occurring mercury ore known as cinnabar.

Illustrations on the treatment of elemental Hg with elemental S are found at (8), http://digital.csic.es/bitstream/10261/7692/1/DISPOSAL%20ELEMENTALHg.pdf; www.clu-in.org/download/contaminantfocus/mercury/sulfur-polymer-22164.pdf.

Example 4: Landfill Disposal of S-waste

(a) **Small Quantities**

STOICHIEOMETRIC MIXING and encapsulation with alkaline products apply to the disposal of small quantities of S-waste. The weight of alkaline product in the mixture per each kilogram of sulphur is (detail in section 4.1)

- 3.2 kg for limestone (calcium carbonate)
- 2.4 kg for hydrated lime (calcium hydroxide)
- 1.8 kg for quick lime (calcium oxide)

Specific spent sweetening agents such as spent iron sponge are pyrophoric and should be kept moist and/or prevented from contacting air (under uncontrolled conditions all the time) once they are removed from the absorption tower beds.

When the alkaline product used is not a pure substance i.e. 100% lime Ca(OH) or 100% CaCO₃ (limestone) then the ANC (or the calcium carbonate equivalent) of the product has to be determined and the quantities and/or thickness of the actual alkaline product adjusted accordingly.

To illustrate, suppose that we have only limestone that has a calcium carbonate equivalent of only 50%. In this case we would need for each kilogram of S

- 6.4 kg for limestone (calcium carbonate)
- 4.8 kg for hydrated lime (calcium hydroxide)
- 3.6 kg for quick lime (calcium oxide)

The layers of alkaline material referred to in section 6.1 and 6.2 would have to be doubled as well.

NOTE: The quantities of alkaline product used may be also adjusted to take into account the ANC inherent to the S-waste or S-containing soil, if any. However, the thickness of the layers of alkaline product should not be reduced when the total S content of the soil or waste exceeds 4%.

(b) <u>Large Quantities of Unrecoverable Sulphur or S-Containing Soil</u>

ENCAPSULATE THE S-WASTE within a casing of alkaline product as described in section 6.2. Dispose of S-waste in consecutive alternating layers of S-waste and alkaline product and in end encapsulated the overall mass as described in section 6.2. This approach is suitable when disposing of large quantities of S-waste constituted by S-containing soil, S block base pad material, or any other S-waste with unrecoverable S.