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## Oxidation of an elemental S fertilizer product as affected by dispersion and temperature

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### Introduction

The production of high demanding sulfur (S) crops such as canola is increasing in Canadian prairies. Elemental sulfur ( $S^{\circ}$ ) can be used as a sulfur source in crop production systems. However, its plant availability over the short term may be low and variable as it must be oxidized by soil microorganisms to  $SO_4^{2-}$ -S to become plant available. Lack of moisture and low temperature in prairie soils can restrict  $S^{\circ}$  oxidation (Janzen and Bettany 1987 a).

Because the surface of  $S^{\circ}$  particles acts as the location for microbial colonization (Lawrence 1987), the conversion rate of  $S^{\circ}$  to  $SO_4^{2-}$ -S is also strongly dependant on the size of  $S^{\circ}$  particles (Janzen and Bettany 1986; Janzen and Bettany 1987 b; Janzen 1990). Fertilizer technology has concentrated on reducing  $S^{\circ}$  particle size and increasing the dispersibility of  $S^{\circ}$  product after application to soil. SulFer95 is a new  $S^{\circ}$  fertilizer. Typical specifications for SulFer95 is that 100% of the particles < 0.074 mm in diameter and 95% of the particles < 0.044 mm (Fernz Sulfur Works Inc. 1996). In the manufacturing process minute  $S^{\circ}$  particles are formed into durable fertilizer size granules using a safe, water soluble binder to facilitate transportation and application. Quantifying the production of  $SO_4^{2-}$ -S from oxidation of Sulfer95 in both intact and dispersed forms under different temperature regime will provide information helpful in

determining how application strategy and environmental conditions may affect plant availability of the fertilizer over time.

This research summarizes a laboratory incubation experiment, examining the influence of temperature and dispersion on oxidation of Sulfer95 to  $\text{SO}_4^{2-}\text{-S}$  in two Saskatchewan soils.

## Material and Methods

**Experimental design:** The experiment consisted of two treatments. The treatments involved two soils, each receiving the intact granules and water dispersed Sulfer95 at rates of 500 and **3000** mg S kg<sup>-1</sup> soil, respectively. A control without S amendment was included. Each treatment was replicated three times. Incubation temperatures were set at **5°**, **10°** and **20°** C.

**Soils:** **One soil** from the Brown soil zone was collected near Central Butte, SASK. The soil is classified as an Orthic Brown Chernozem mapped as Haverhill association of sandy loam texture. Another soil from the Black soil zone was collected from a farm field about 15 km south of Prince Albert, Sask. The soil at the site is classified as an Orthic Black Chernozem (Meota association) of loam texture. Both are common soil types within the respective soil zone which had no history of S fertilization. The samples (0-10 cm) were collected from a rotation phase so as to have low soluble sulfate contents and were air dried and passed through 2 mm sieve before incubation. Related properties of the soils are presented in Table 1.

**Table 1. Characteristics of the two Saskatchewan soils used in the incubation experiment.**

Parameters	unit	Haverhill	Meota
Clay	%	18	26
Silt	%	26	33
Sand	%	56	41
Total N	g kg <sup>-1</sup>	1.5	3.79
organic c	g kg <sup>-1</sup>	16.4	42.3
organic s	g kg <sup>-1</sup>	0.11	0.44
(NH <sub>4</sub> <sup>+</sup> + NO <sub>3</sub> <sup>-</sup> )-N	mg kg <sup>-1</sup>	4.12	15.9
Extractable P	mg kg <sup>-1</sup>	5.89	4.99
Extractable K	mg kg <sup>-1</sup>	69.9	76.6
Extractable SO <sub>4</sub> <sup>-2</sup> -S	mg kg <sup>-1</sup>	2.00	2.31
E. C.	mS cm <sup>-1</sup>	672	600
pH		8.19	7.51

**Sulfur: Uniform** intact fertilizer granules of Sulfer95 were obtained by retaining the portion that passed through a 6 mesh sieve (diameter 3.36 mm) but not a 12 mesh sieve (1.68 mm). To obtain the dispersed form, the Sulfer95 was placed in water over night and sieved through a 325 mesh sieve (0.044 mm). The S<sup>o</sup> particles that passed through the sieve were placed in a oven at 45 °C to dry. During drying, the semi-lumpy S<sup>o</sup> was gently crushed manually and then re-screened through a 325 mesh sieve. Particles passing through the sieve were collected and used in the experiment.

**Incubation:** A 7.5 cm diameter filter funnel with a detachable tip was used for incubation. A piece of glass fiber filter paper was placed on the bottom of the **funnel**, and 75 g of soil was

added. The  $S^o$  fertilizer in dispersed form was weighed and distributed evenly across the **soil surface**. The **granular  $S^o$**  was distributed the surface at random using a plastic stick. Another 75 g of soil was used to cover the fertilizer treatments. After a glass filter paper was placed on the soil surface, 40 and 45 ml aliquots of water were added to Haverhill and Meota soils, respectively. This procedure adjusted the moisture content of the soils to 60% of their field capacity. Each funnel was kept in a 2 L plastic container and a piece of filter paper was placed on the bottom of the container and wetted with water to maintain the moisture content. The containers were then sealed and placed in three different incubation chambers, each with a controlled temperature set at 5, 10 and 20 °C, respectively. The total number of containers was 90.

Every two days, the lid of each container was opened for aeration. Every two weeks, the funnels were taken out of chamber, the tips were installed and the funnels were placed on a vacuum suction apparatus within which a scaled cylinder was used to collect leachate. A 100 ml aliquot of  $CaCl_2$  (0.001 M) was used to leach  $SO_4^{2-}-S$  out of the soil. A slight vacuum was applied to adjust the volume of leachates to be 100 ml at the end of each leaching. Then, the funnels were returned to the incubation chamber for another two-week incubation and the leaching procedure was repeated. The content of S in leachates was determined for its S content.

**Analytical methods:** Soil texture was analyzed using the pipette method (Green 1978). Soil was treated with HCl to remove inorganic C, then organic C, total N and S were analyzed using a Leco CNS 2000 Elemental Analyzer (Leco Instruments Limited, Mississauga, Ontario, L5T 2H7). Soil  $NH_4^+-N$  and  $NO_3^- -N$  were extracted with 2 M KCl and determined colorimetrically (Keeney and Nelson, 1982). Soil  $SO_4^{2-}-S$  was extracted with  $CaCl_2$  (0.01M). The extracts from the soil and the leachates from leachates were analyzed for  $SO_4^{2-}-S$  using

Inductively Coupled Plasma Spectroscopy (Model **3410+ICP** Spectrometer, Applied Research Laboratories, 24911 Avenue Stanford Valencia, California, 913559960). Available soil P and K were evaluated using a modified Kelowna method (Qian et al. 1994). The soil pH was determined in a soil water paste (Byers 1978). Statistical analysis of the data and modeling of **S°** oxidation were conducted using SAS program (SAS Institute Inc. 1990).

## **Results and Discussion**

The oxidation of **S°** is measured as  $\text{SO}_4^{2-}\text{-S}$  extracted from the soil by **0.001M CaCl<sub>2</sub>** over consecutive leachings. The actual amount of **SO<sub>4</sub><sup>2-</sup>-S** produced from **S°** during a two-week incubation was calculated as the difference between the **S°** treatment and a control under the same temperature conditions. The total cumulative production of **SO<sub>4</sub><sup>2-</sup>-S** from the **S°** application is presented in Table 2.

**Table 2. Percentage of elemental S (S°) oxidized during 10 weeks incubation as influenced by temperature, soil type and application rate.**

Temp (°C)	Appl. Dose (mg S kg <sup>-1</sup> soil)	S° forms	(% of S° recovered as SO <sub>4</sub> <sup>-2</sup> -S)	
			Haverhill	Meota
5	500	Intact	1.0	1.0
		Dispersed	16.5	6.0
	3000	Intact	1.9	1.2
		Dispersed	9.5	5.0
10	500	Intact	3.8	3.0
		Dispersed	31.1	20.7
	3000	Intact	3.5	3.9
		Dispersed	18.0	10.5
20	500	Intact	7.0	9.4
		Dispersed	59.9	51.7
	3000	Intact	7.9	7.4
		Dispersed	29.7	37.8

In general, **only** a small portion of S° (<10%) in intact form was oxidized during the 10 weeks incubation, especially at low temperatures. At 20 °C, about 7 to 9 % of S° was oxidized in comparison with 1% at 5 °C. Under the same temperature conditions, the percentages of intact S° oxidized **were** similar, indicating that the oxidation of intact granules was not affected by soil type or the rate of application.

At any given temperature, production of SO<sub>4</sub><sup>-2</sup>-S from dispersed S° was much higher than that of intact. Dispersion significantly enhanced oxidation. However, the percentage of S° oxidized appeared lower at the rate of 3000 mg kg<sup>-1</sup> than the rate of 500 mg kg<sup>-1</sup> at all three

temperatures, which implies that the  $S^0$  oxidation was somewhat inhibited by increasing the rate. The percentage of  $S^0$  oxidized differed between the two soils, although it was not consistent under all temperature regimes. At 5 and 10 °C, less  $S^0$  oxidized in Meota than in Haverhill soil at both application rates while at 20 °C, less  $S^0$  was oxidized in Haverhill than in Meota at the application rate of 3000 mg  $kg^{-1}$ .

As it has been reported that the optimum soil moisture for  $S^0$  oxidation may be at 100% field water holding capacity, the oxidation rates at 60% of field capacity used in this experiment may not be restricted. However, moisture content of less than 100% field water holding capacity probably better reflects the soil moisture status near the soil surface in the semi-arid Canadian prairie.

In non-calcareous, non-saline mineral soils, organic matter contains more than 95% of the S in surface horizons, such that the release of S from organic matter mineralization is very important for S fertility (Tabatabai and Bremner 1972, Bettany et al. 1979). The contribution of mineralized S from organic matter decomposition should be taken into consideration in this study, because the soil contained low  $SO_4^{2-}$ -S concentration and relatively high concentration of organic C (Table 1). Soil organic matter mineralization could be inhibited to some extent initially by application of  $S^0$ . In a laboratory incubation, Sulewski (1997) observed that soil  $CO_2$  evolved was lowered as a result of  $S^0$  addition, suggesting slower organic matter decomposition. Because the method used to calculate  $S^0$  oxidation assumes an equal production of  $SO_4^{2-}$ -S from soil organic matter decomposition for all treatments, less  $SO_4^{2-}$ -S contribution from the soil applied with  $S^0$  would result in underestimation of the  $SO_4^{2-}$ -S released from oxidation.

‘An empirical model based on a first order relationship was found to provide the best fit in

depicting the cumulative oxidation of  $S^o$  during the incubation period.

$$S_t = S_0 \cdot [\exp(kt^n) - 1] \dots\dots (1)$$

Where  $S_t$  is cumulative  $SO_4^{2-}\text{-S}$  (mg) production from  $S^o$  after time t, and t (week) is the time. The  $S_0$  is the amount of  $S^o$  (mg) added to soil when t = 0. The k and n are constants calculated by fitting the cumulative  $SO_4^{2-}\text{-S}$  production measured at different times using SAS program (SAS, 1990). For intact and dispersed  $S^o$  at the application rate of 500 mg  $kg^{-1}$ , the fitted curves in the two soils are presented in Fig. 1. The values of the parameters k and n under different temperatures are presented in Table 3.

Janzen and Bettany (1987 a) found that the relationship between  $S^o$  oxidation rate and incubation temperature can be described using the following equation:  $k=a \cdot b^T$ ; where k is oxidation rate; a, b are constants, and T is temperature. The following equation is developed to incorporate temperature effects.

$$S_t = S_0 \cdot [\exp(kt^n) - 1] \cdot a^T \dots\dots\dots (2)$$

Where a is a constant and T is temperature. The K, n and a values were calculated using the SAS program described above and are listed in Table 3. To verify the precision of the equation, the predicted values under different temperatures were calculated using equation 2 and the parameters listed in Table 3, and were compared to the actual measured values. The correlations between predicted and measured values are presented in Fig.2. The highly correlated relationships indicate that the oxidation of  $S^o$  in intact and dispersed forms under different temperature regimes can be adequately described and predicted using equation 2.



**Table 3. Parameters calculated for describing S° oxidation under different temperatures using a modified first order equation.**

<b>A. Parameters for equation 1</b>								
<b>S° Forms</b>	<b>Haverhill</b>					<b>Meota</b>		
	<b>Temp</b>	<b>(°C)</b>	<b>k</b>	<b>n</b>	<b>a</b>	<b>k</b>	<b>n</b>	<b>a</b>
<b>Intact</b>	<b>5</b>		<b>0.0012</b>	<b>0.898</b>		<b>0.0021</b>	<b>0.658</b>	
	<b>10</b>		<b>0.0002</b>	<b>2.240</b>		<b>0.0007</b>	<b>1.361</b>	
	<b>20</b>		<b>0.0044</b>	<b>1.219</b>		<b>0.0027</b>	<b>1.524</b>	
<b>Dispersed</b>	<b>5</b>		<b>0.0021</b>	<b>0.658</b>		<b>0.0026</b>	<b>1.349</b>	
	<b>10</b>		<b>0.0007</b>	<b>1.361</b>		<b>0.0010</b>	<b>2.296</b>	
	<b>20</b>		<b>0.0027</b>	<b>1.524</b>		<b>0.0452</b>	<b>0.986</b>	

**R<sup>2</sup> >0.95 and P<0.001** for all above equations.

<b>B. Parameters for equation 2</b>							
<b>Intact</b>	<b>5-20</b>	<b>0.0005</b>	<b>1.32</b>	<b>1.1086</b>	<b>0.0001</b>	<b>1.55</b>	<b>1.1755</b>
<b>Dispersed</b>	<b>5 - 20</b>	<b>0.0117</b>	<b>0.88</b>	<b>1.1034</b>	<b>0.0028</b>	<b>1.18</b>	<b>1.1365</b>

### **Conclusion**

The oxidation production of Sulfer95 is sensitive to dispersion and temperature. The S° oxidation is greatly increased when the S° is applied in dispersed form. The highest production of S° oxidation was obtained at the high temperature (20 °C) with dispersed form at the low rate. Enhanced dispersion of elemental S, resulting from surface broadcast applications in the fall or early spring, is expected to favor greater oxidation.

The cumulative production of SO<sub>4</sub><sup>-2</sup>-S from Sulfer95 can be described by an empirical equation.

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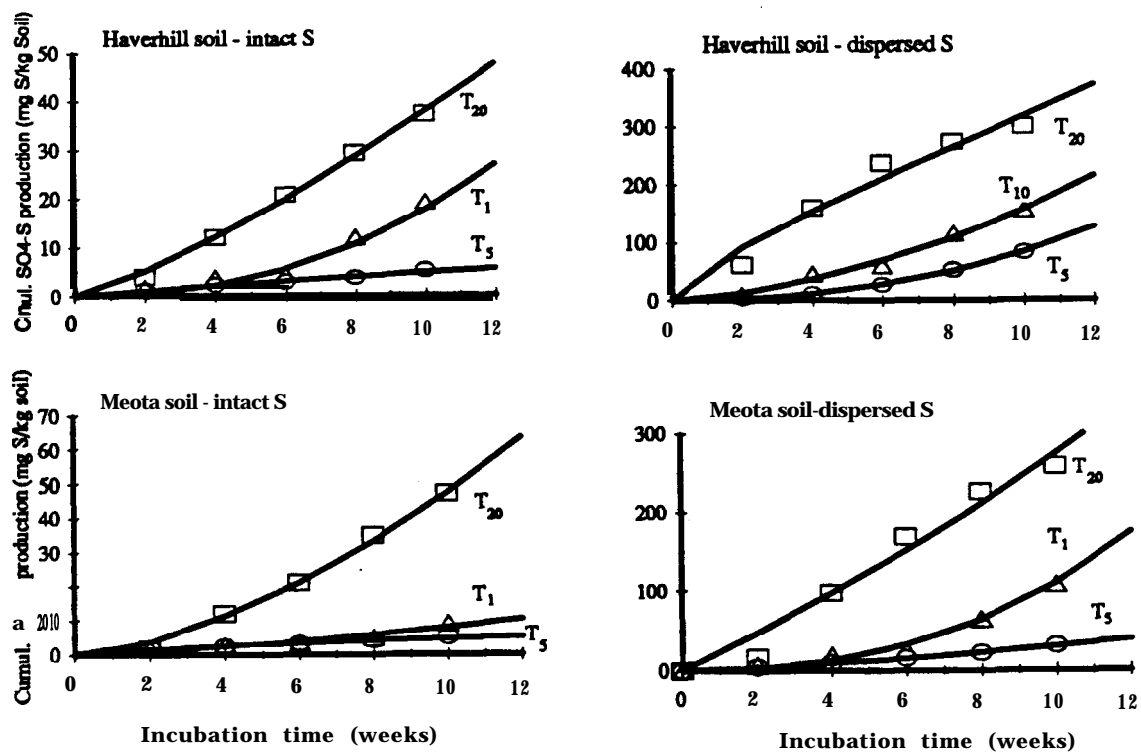
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**Fig. 1. Cumulative  $\text{SO}_4^{2-}\text{-S}$  production from oxidation of Sulfur95 (in intact and dispersed forms) in Haverhill and in Meeta soils as influenced by temperature.**

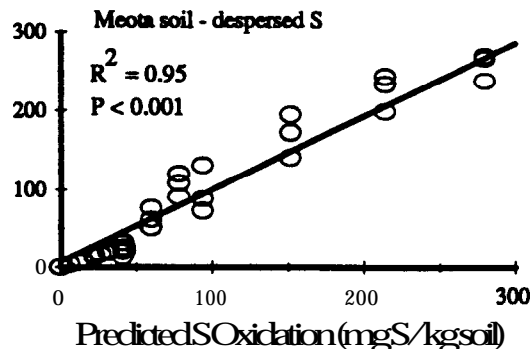
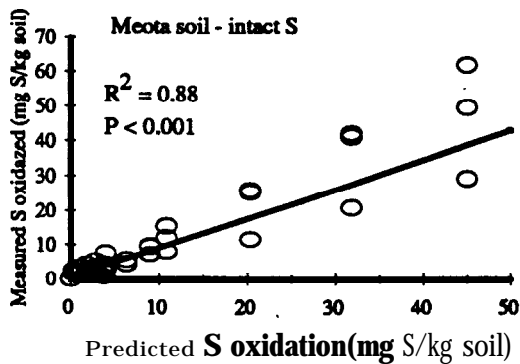
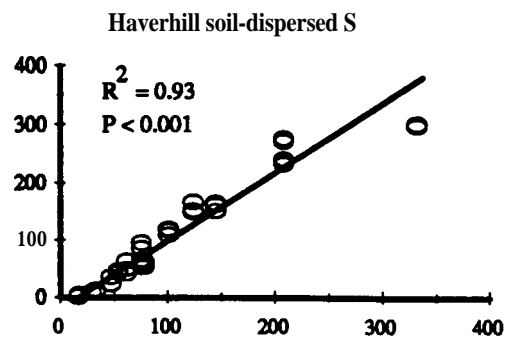
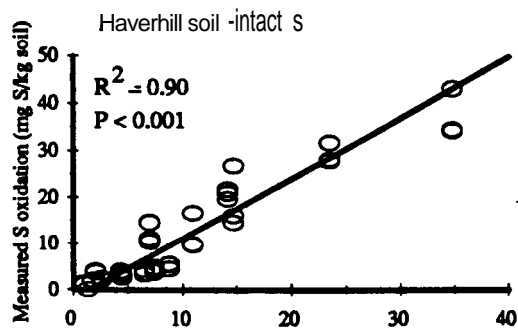


Fig.2. Correlations between predicted and measured Sulfer95 (in intact and dispersed forms) oxidation production in Haverhill and Meota soils.