

# Elemental Sulfur Combinations and Regional Waste Gypsum Products as Alternative Sulfur Fertilizer Sources.

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## Abstract

The potential of elemental sulfur and gypsum as viable sulfur alternatives to ammonium sulfate were evaluated. Continued concerns regarding poor product performance by elemental sulfur, and the lack of an economically viable gypsum source have restricted large scale usage. Laboratory and field measurement of plant available S release, plant yield, residual soil sulfate, and crop use efficiency suggest advantages to sludge plus elemental sulfur usage rather than application of elemental sulfur alone. Altering elemental sulfur's physiochemical nature leads to inherent advantages in microbial establishment, which is the initial process critical to the conversion of  $S^0$  to sulfate. The final product is envisioned as a fertilizer pellet or prill utilizing sludge as a binder or carrier agent. The tested waste gypsum products are sulfate alternatives with solubilities that predict short-term to intermediate availability. Waste gypsum products have specific advantages in certain environmental niches wherein readily soluble fertilizers could be lost to leaching and immobilization.

**Key Words:** elemental sulfur, sludge, regional waste gypsum, enhancement, economically viable

## 1.0 Introduction

Producers in western Canada are quite restricted in their choice of effective sulfur fertilizers to address rising fertilizer costs. Elemental sulfur usage has resulted in less than optimal performance in our prairie climate (Janzen and Bettany 1987). It's oxidation rate is slow at typical fertilizer prill sizes, and are difficult to apply in finely divided formats (Karamanos and Janzen 1991). Other less soluble sulfate sources, such as gypsum, have been considered (Harapiak 1980) but their limited supply to producers has restricted widespread evaluation and application. The combining of Saskatoon's dried digested sewage sludge (DDS) with elemental sulfur to enhance sulfur oxidation, and the utilization of regional waste gypsum (ie. wallboard and mining by-product ore) are possible solutions to these concerns.

The goals of this research were: (1) identification of elemental sulfur combinations with sufficient promise to warrant field application, (2) provision of insight into the mechanisms responsible for enhanced sulfate release from  $S^0$ + DDS combinations, and (3) assessment of the efficacy of elemental sulfur combinations and regional waste gypsum with canola in the year of application.

## 2.0 Materials and Methods

### 2.1 Laboratory

**Methods** regarding soil incubation and growth chamber experiments were published in the previous Soils and Crops proceedings (Sulewski and Schoenau 1995); however, soil incubation data have been amended (two additional weeks) to represent the full duration of the experiment. An estimation of particle size diameter for each  $S^0$  containing combination was attained by microscopic analysis.

### 2.2 Field Study

The study was conducted in east-central Saskatchewan near Star City. The soil was a sulfur deficient Gray Luvisol silt-loam mapped as a Porcupine - Kamsack complex (Saskatchewan Soil Survey, 1989). Elemental sulfur mixture preparation followed the procedure as outlined previously (**Sec.2.1**) and differed only in terms of scale. Plots were established on May 9th / 95 and the treatments were broadcast on standing wheat stubble. The study area had received 100 lbs N  $\text{ac}^{-1}$  the previous fall as anhydrous ammonia.

Treatments were applied at three rates (20,40 , and 80 kg S  $\text{ha}^{-1}$ ). Elemental sulfur and gypsum treatments had additional N applied as ammonium nitrate at rates equivalent to levels supplied by ammonium sulfate. An ammonium nitrate control treatment (0 S) was also included at each of the three application rates. The products were incorporated by a cultivator the following day, and canola (*Brassica napua* L. cv. Garrison) was seeded with an International 7400 hoe-drill on May 16th. Soil samples (0 - 15cm) were taken from each of the control plots at emergence on June 1st to establish initial sulfate status.

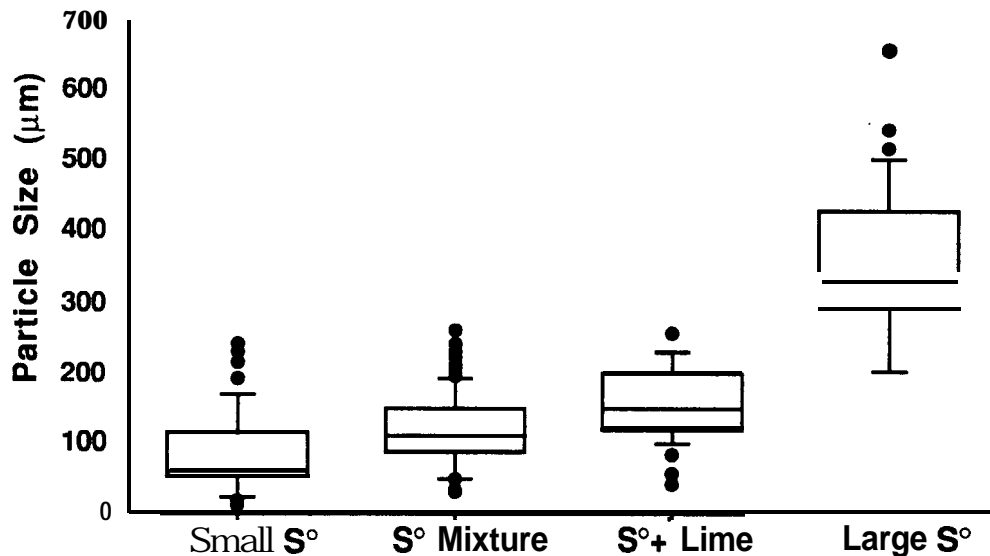
Mid-season biomass samples were taken on July 24th when the plants were in full flower. Whole plants contained in a 0.25 sq m quadrat (duplicate) were randomly sampled from each plot. The samples were dried (40°C), weighed, and finely ground in preparation for plant tissue S and N analysis through combustion by a Leco CNS - 2000 analyzer. Final yields and plant samples were obtained on August 3 1st using a one square meter sampling area. After harvest, plant samples were allowed to ripen naturally, and were weighed (total plant yield) and threshed. Seed weights were recorded and subsamples of the seed and straw were respectively ground with a ball-mill and Cyclone™ grinder for S and N analysis through combustion.

Soil samples were taken on September 16th from each plot (four samples / plot, 0 - 30cm) which were bulked, air-dried, and ground. Residual sulfate was determined through a 0.01M  $\text{CaCl}_2$  extraction.

### 3.0 Results

#### **3.1 Elemental Sulfur Particle Size Distribution**

Two distinct size distributions were created from a commercially available  $\text{S}^0$  product, and are represented by the small  $\text{S}^0$  and large  $\text{S}^0$  box-plot diagrams (Figure 3.1). All experiments were conducted with the finely divided  $\text{S}^0$ .

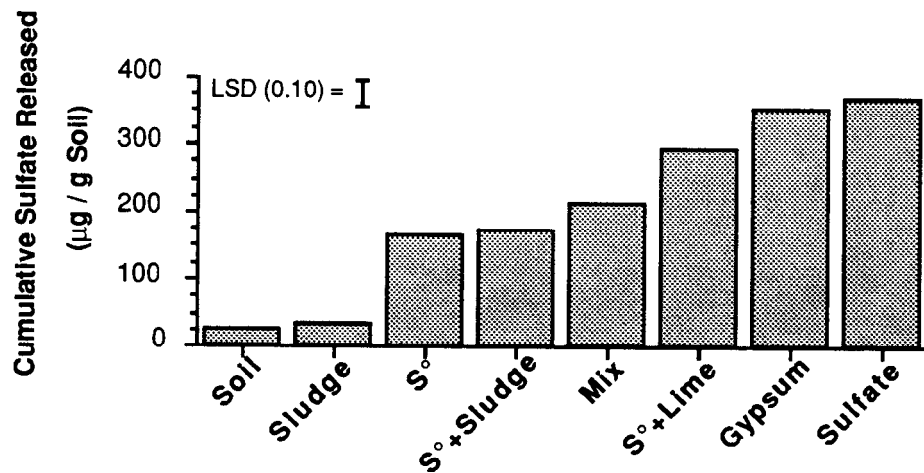


**Figure 3.1** Size distributions of  $\text{S}^0$ , [ $\text{S}^0$ + lime], and the  $\text{S}^0$  Mixture.

Box-plots of the small  $S^0$ ,  $S^0$  mixture, and  $S^0$  + lime show a steady increase in the mean particle diameter, which was a consequence of  $S^0$  surface coating and aggregation of extremely small  $S^0$  particles with DDS and lime.

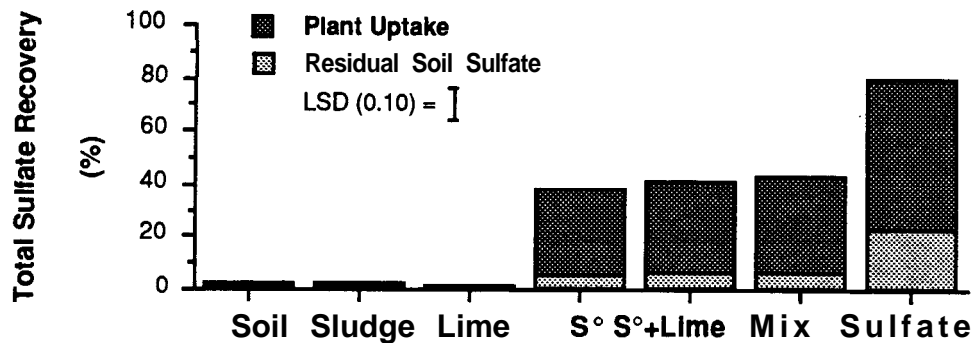
### 3.2 Laboratory Experiments

The 12 week data (Figure 3.2) provides similar results to the 10 week data previously presented (Sulewski and Schoenau 1995). The sulfate source provides the highest release; however, the gypsum treatment (wallboard) is comparable over the 12 week period. In comparison to  $S^0$  alone, only the  $S^0$  mixture and  $S^0$  + lime combination were capable of significantly increasing sulfate release



**Figure 3.2** Cumulative  $CaCl_2$  extractable sulfate (12 weeks) for sulfur sources added to a Sylvania silt loam soil.

In the growth chamber, the sulfate source provided much higher plant uptake and residual soil sulfate levels than all  $S^0$  combinations when products were applied at  $100 \mu g S g^{-1}$  soil (Figure 3.3). Despite the lack of significant difference amongst  $S^0$  treatments, yields obtained from the complete mixture were significantly higher ( $P \leq 0.10$ ) than  $S^0$  alone.



**Figure 3.3** Sulfate recovered from powdered  $S^0$  and sulfate sources.

The comparison between sulfate and waste wallboard gypsum recovery (Figure 3.4) also shows sulfate to be superior, as the respective total sulfur recoveries are approximately 80% and 50%. Despite this difference, yields between the sources were not significantly different.

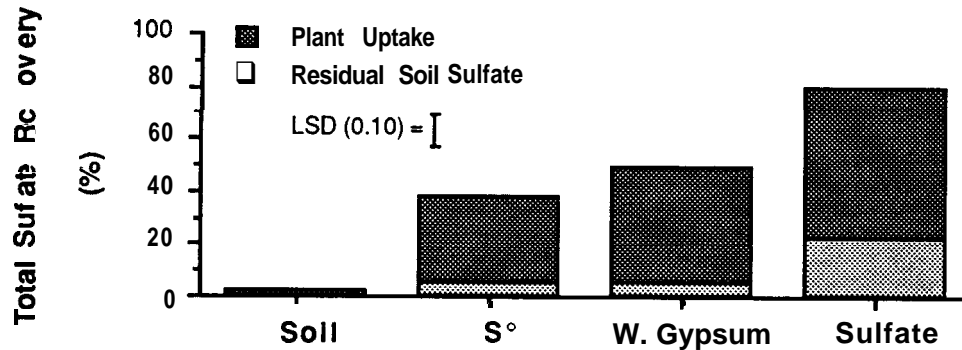


Figure 3.4 Sulfate recovered from powdered S°, gypsum, and ammonium sulfate.

### 3.3 Field Study

Soil samples (0 - 15cm) showed marginally deficient SO<sub>4</sub>-S levels (8.4 kg ha<sup>-1</sup>) at the time of crop emergence. A significant S uptake response to added sulfur was obtained at the both mid-season (full flower) and season's end (Figure 3.5). Total S uptake values represented by straw (dark) and seed (light) reveal two distinct groups which include: (1) all S° combinations, and (2) all sulfate sources. Ammonium sulfate provides the highest values; however, wallboard gypsum is not significantly different ( $P \leq 0.05$ ). No significant difference exists amongst the three S° combinations.

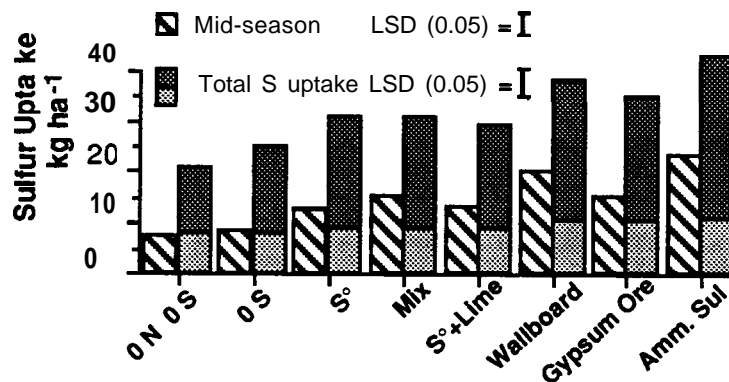
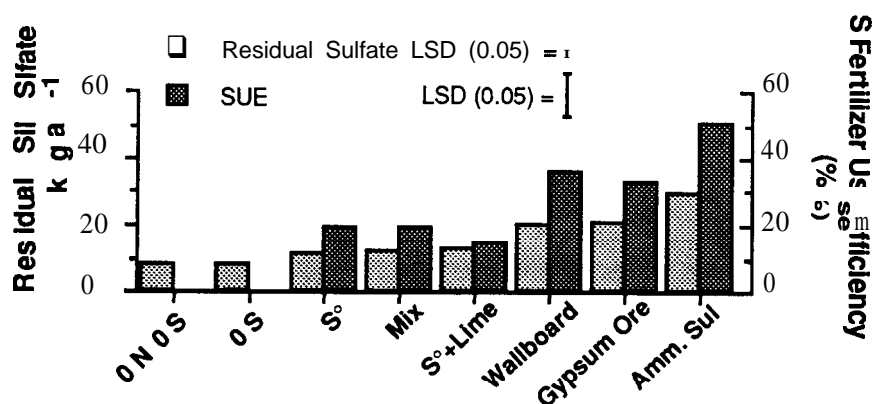


Figure 3.5 Source comparison of sulfur uptake at mid-season and harvest.

Examination of both residual soil sulfate (0 - 30cm) and sulfur fertilizer use efficiency (SUE) reveals a three tiered response (Figure 3.6). Ammonium sulfate provided significantly higher values ( $P \leq 0.05$ ) (ie. 25 kg SO<sub>4</sub>-S ha<sup>-1</sup>, 50% SUE). Both waste gypsum products (wallboard gypsum and by-product gypsum ore) provided intermediate levels of residual soil sulfate and SUE, while the S° combinations were the least efficient.



**Figure 3.6** Source comparison of residual soil sulfate and fertilizer use efficiency.

Mid-season biomass yields (Table 3.1) showed a significant response to S application; however, ammonium sulfate was the only treatment with yields significantly higher than  $S^{\circ}$  alone ( $P \leq 0.05$ ). Despite a  $0.41 \text{ T ha}^{-1}$  ( $7.1 \text{ bu ac}^{-1}$ ) difference between the ON OS and ammonium sulfate treatments, final grain yields showed no significant response to sulfur application.

**Table 3.1** Mid-season biomass and final grain yield as related to S source.

S Source	Dry Matter Production	
	Mid-Season Biomass	Grain Yield
	$\text{T ha}^{-1}$	
ON OS	1.62	1.62
OS <sup>§</sup>	2.16	1.63
$S^{\circ}$	2.79	1.78
$S^{\circ}$ Mixture	2.91	1.79
$S^{\circ}$ + Lime	2.98	1.85
Wallboard	3.09	2.02
Gypsum Ore	3.09	2.02
Amm. Sulfate	3.29	2.03
LSD (0.05)	0.52	NS <sup>†</sup>

<sup>†</sup> F value for the model not significant.

<sup>§</sup> Ammonium nitrate application equivalent to N supplied by ammonium sulfate.

## 4.0 Discussion

### 4.1 Elemental Combinations

Two goals are in mind when considering the combining of  $S^{\circ}$  with DDS. The first goal

relies on DDS as a binder or carrier agent for finely divided  $S^0$  powders. Similar products include two fertilizer amendment products developed in Italy (Ceccotti 1994). These organically registered products are composed of finely divided  $S^0$  (90% - 95% < 100 $\mu$ m) combined with organic manures and an unnamed binding agent. These mixtures are reported to yield dust-free, pelleted materials that break-down under the presence of moisture.

The second goal relies on foreseen chemical and microbiological properties advantageous to  $S^0$  oxidation. Enhancement of  $S^0$  oxidation rate is well documented through addition of substrates with high organic C concentrations (Wainwright et al. 1986; Lawrence and Germida 1988; Cifuentes and Lindeman 1993). Evidence of ample nutrient supplying power and concentrated populations of micro-organisms (Cowell and deJong 1991; Hulit 1991) suggest advantages in  $S^0$  to sulfate conversion due to DDS inoculation abilities.

As an  $S^0$ + DDS mixture some degree of buffering against detrimental pH declines have been observed (Cowell and Schoenau 1995). The addition of hydrated lime is viewed as a solution to further extend  $S^0$  oxidation rates. Evidence in this study showed  $S^0$  surface coating and particle aggregation with addition of hydrated lime (Figure 3.1). Subsequent addition of DDS resulted in surface staining and incorporation of organic materials within the surface of  $S^0$  particles to the degree that viable fungal hyphae were visibly attached to these altered surfaces. Previous studies have indicated  $S^0$  surface coating with humic-like material is an essential precursor to microbial establishment due to their ability to reconfigure surface properties as well as provide readily accessible nutrients (Lawrence 1987).

#### **4.2 Waste Gypsum Products**

**The** main advantage in gypsum application is largely a function of cost; however, it's properties are particularly well suited to certain environmental niches. The availability of gypsum is largely restricted by it's solubility, which is significantly lower than readily soluble ammonium sulfate. Reduced solubility dictates reduced release rates and suggest possible advantages in soils prone to conditions which favor leaching and immobilization of readily available fertilizers.

A common trait of S deficient Gray Luvisolic soils is a low content of basic cations such as calcium. A result of this low base saturation would be slight enhancement of gypsum solubilization. In addition to increasing S fertility the practice of using gypsum for improvement of soil physiochemical properties such as structure, sodicity, and phosphorus availability are well documented (Wallace 1994).

### **5.0 Conclusions**

The effectiveness of finely divided  $S^0$  can be improved with the addition of Saskatoon's dried digested sewage sludge (DDS) and hydrated lime. Evidence in the laboratory suggests a more hospitable surface for microbial colonization on  $S^0$  was created due to surface coating with lime, and incorporation of organic material into this coating. Despite evidence supporting enhanced  $S^0$  to sulfate conversion in the lab, field results are inconclusive. Definite handling advantages for  $S^0$ + DDS exist due to reduced dust accumulation, which contributes to  $S^0$  unsuitability for large-scale field application.

Both lab and field data suggest advantages for the use of the waste gypsum products. Both wallboard gypsum and gypsum by-product ore are intermediately available sources, which compare well to ammonium sulfate.

### **Acknowledgment**

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