

1 UPLAND ACID SULFATE SOILS AND THE EFFECT OF SULFIDE  
2 OXIDATION ON SOIL GENESIS IN SASKATCHEWAN SOILS, CANADA

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10 SUMMARY

11 Recent studies on upland acid sulfate soils in east central  
12 Saskatchewan generated interest in further study of sulfide oxidation  
13 and its effect on soil salinity, soil acidity, Solonetzic soil forma-  
14 tion and other soil properties. Objective of this study was to under-  
15 stand the effects of sulfide oxidation on soil properties, especially  
16 the formation of sulfate salts using chemical, x-ray diffraction and  
17 scanning electron microscope techniques. Field and laboratory studies  
18 indicated that pyrite and jarosite were also widespread occurrences in  
19 southern Saskatchewan. Extremely high concentration of sulfate salts  
20 (mirabilite, thenardite, bloedite, konyaite, loewite, gypsum) were  
21 found in the depressions where the sulfide oxidation process was  
22 dominant in the subsoils. Presence of Solonetzic soils in higher  
23 elevations suggests their association to saline soils. Sulfide oxida-  
24 tion are likely responsible for most of the free iron oxides and iron  
25 substitution in smectites in Saskatchewan soils.

## INTRODUCTION

1  
2           Recent studies (Curtin and Mermut, 1985; Mermut et al. 1985)  
3 in east central Saskatchewan have indicated the presence of upland  
4 acid sulfate soils with characteristic features of acid sulfate  
5 weathering in the province. These soils were derived from the pyrite-  
6 bearing Cretaceous marine shale and showed the presence of jarosite as  
7 a result of pyrite oxidation. Further field and laboratory studies  
8 revealed that these soils are also present in southern Saskatchewan  
9 and have considerable amounts of sulfate salts and low pH. Increase  
10 in soluble salts due to sulfide oxidation in coastal acid sulfate  
11 soils is quite well established (Ponnamperuma et al., 1972; Marius,  
12 1982). However, no information is available on the salt production by  
13 sulfide oxidation in upland soils.

14           Solonetzic soils in Saskatchewan, especially the Solods,  
15 occur on the glacial deposits highest in Cretaceous marine shale  
16 (Mitchell et al., 1944) and in areas where sulfate salts are concen-  
17 trated. Moreover complete oxidation of sulfides produce free iron  
18 oxides (Van Breeman, 1982) and effect the nature of clay minerals  
19 forming more iron rich smectites (Mermut et al., 1984; Van Breeman,  
20 1976).

21           Objectives of the present study were: (i) to establish the  
22 pathways between sulfide oxidation and formation of sulfate salts,  
23 (ii) to understand the effect of sulfide oxidation on soil properties.

## MATERIALS AND METHODS

24  
25           Several deep soil columns were examined by a hydraulic auger

1 on the Souris River plain (Township 11, Range 14, west of the second  
2 meridian), about 25 km north of Weyburn south eastern Saskatchewan,  
3 Canada. Major soils of the region are Solonetzic soil (Mitchell,  
4 1944). Two profiles were included in this study. The composition of  
5 the thin till mantle (1.0-1.5m) is influenced by the underlying shale  
6 and the shale content increases with depth. The shale between 1 and  
7 6m depth has pale yellow veinlets and splotches and low pH. These  
8 were attributed to sulfide oxidation and recognized as oxidized zone.  
9 Below 6m the soil color was black and without mottles. This zone is  
10 the reduced zone with permanent water table.

11           The samples with yellow streaks were immediately examined for  
12 the presence of jarosite by x-ray diffraction (XRD) analysis after  
13 they had been dispersed ultrasonically. A Philips 505 Scanning  
14 Electron Microscope (SEM) was used to determine the submicroscopy of  
15 jarosite and associated pyrite, gypsum, and other more soluble sulfate  
16 salts.

17           Undisturbed soil samples were kept in moist state in plastic  
18 bags and saturation paste was prepared for immediate measurement of pH  
19 and soluble salts. pH and electrical conductivity (EC) were deter-  
20 mined in saturation extract. Sodium,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$  were analysed by  
21 atomic absorption spectrophotometry,  $SO_4^{2-}$  was by the  $BaSO_4$  precipi-  
22 tation method and  $HCO_3^-$  and  $CO_3^{2-}$  were by titration techniques. Total  
23 carbon was determined by dry combustion, inorganic carbon by HCl  
24 dissolution, with difference between the two representing the organic  
25 carbon. Free iron were determined by atomic absorbtion spectroscopy

1 using the citrate-dithionite-bicarbonate (CDB) extraction of Mehra and  
2 Jackson (1960).

### 3 RESULTS AND DISCUSSION

#### 4 XRD and SEM Studies

5 XRD of yellow streaks from the oxidized zone (1-6m) and the  
6 dark colored rounded nodules isolated with the help of binocular  
7 microscope from the reduced zone (>6m) verified the presence of jaro-  
8 site and pyrite respectively. Apparently no pyrite was present in the  
9 oxidized zone. Gypsum was present in both the oxidized and reduced  
10 zones.

11 Shape and size analysis of the samples from the reduced zone  
12 by SEM examinations verified the presence of individual 5-30 $\mu$ m sized  
13 well developed crystals in large cavities with the perfect octahedral  
14 morphology of isometric crystal system (Fig. 1). Under higher magni-  
15 fication, however, many etch pits were observed (Fig. 2) on the sur-  
16 face of individual pyrite crystals indicating their weathering,  
17 despite a high pH in the reduced zone. SEM studies of yellowish  
18 mottles from the oxidation zone showed the presence of jarosite which  
19 had different size and shape than pyrite. The majority of the  
20 jarosite crystals were between 0.1 $\mu$ m and 1.0 $\mu$ m, much smaller than the  
21 pyrite crystals in the unoxidized zone and they were nearly cubic  
22 (Fig. 3). Mermut et al. (1985) suggested that due to the differences  
23 in size, shape and distribution pattern, jarosite is formed by recryst-  
24 tallization from solution.

25

## 1 Origin of Salts

2           Acid sulfate soils occurring in coastal areas are reported to  
3 be saline due to influx of sea water (e.g. Ponnampetuma et al. 1972;  
4 Marius, 1982). In addition to chlorides, considerable amounts of  
5 sulfates were found in recent acid sulfate soils due to oxidation of  
6 pyrite and hydrolysis of jarosite. However, sulfate may be removed  
7 from the soil solution and precipitated as gypsum. Therefore the  
8 contents of  $\text{SO}_4^{2-}$  in soil solution reported for coastal acid sulfate  
9 soils are much less than the contents of  $\text{Cl}^-$ .

10           Analysis of the soil solutions obtained from the two profiles  
11 used in this study (Table 1) indicated that there is an accumulation  
12 of salts in the subsoils. Presence of jarosite and low pH in the  
13 oxidized zone show that the soils are in post sulfurization stage  
14 (Carson et al., 1982). Among the anions  $\text{SO}_4^{2-}$  was almost the only  
15 anion in the salt system. Large quantities of gypsum found in both  
16 the oxidized and reduced zone is an indication of sulfate accumulation  
17 in the soil. This clearly indicates that the oxidation of pyrite in  
18 the Cretaceous marine shale has led to the formation of large quanti-  
19 ties of acid sulfate waters which reacted with calcite and dolomite  
20 and converted large parts of it to gypsum. Formation of acid sulfate  
21 waters in Cretaceous marine shale is quite well established.  
22 (Pettijohn, 1957; Shultz, 1964).

23           The major cation in the salt system was  $\text{Na}^+$ . However,  
24 considerable amounts of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  were also found in the soil  
25 solution. It is known that Cretaceous marine shales in Saskatchewan

1 (Cole, 1926) have  $\text{Na}^+$  as the dominant exchangeable cation. Calcium  
2 and magnesium were likely added to the system through the dissolution  
3 of calcite and dolomite which were present in the till mantle. Preci-  
4 pitation of large amounts of gypsum observed in the oxidized zone and  
5 unoxidized zone, higher  $\text{Mg}^{2+}$  than  $\text{Ca}^{2+}$  in the soil solution were  
6 considered as an indication of this process. There was no secondary  
7 carbonate accumulation zone, however precipitation of large amounts of  
8 gypsum lead to the buildup of  $\text{Mg}^{2+}$  in the soil solution. Higher  
9 soluble  $\text{Mg}^{2+}$  than  $\text{Ca}^{2+}$  is considered to be a clear indication of this  
10 process. Formation of Mg-bearing calcite observed by St. Arnaud  
11 (1978) in the soils formed on glacial till in Saskatchewan is another  
12 indication of  $\text{Mg}^{2+}$  buildup in soil solution.

13           Expression of cations in terms of percentage as indicated in  
14 Table 2 provided a better insight as to the variation in ionic compo-  
15 sition. It seems that there is an increase in soluble  $\text{Na}^+$  with depth.  
16 If the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were produced within the till mantle, their pre-  
17 sence in the lower part of the profile indicates the downward movement  
18 of these cations. More mobile nature of  $\text{MgSO}_4$  especially, under low  
19 temperature, explains the presence of Mg in the oxidized and unoxi-  
20 dized zones. Similar trends were found in percent distribution of  
21 exchangeable cations (Table 3). As a result of cation exchange most  
22 of the exchangeable sodium were therefore converted to the soluble  
23 sodium forming either sodium sulfates along (mirabilite  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ,  
24 thenardite  $\text{Na}_2\text{SO}_4$ ) or in combination with magnesium (bloedite  
25  $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ , konyaite  $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$  and loeweite

1  $\text{Na}_{12}\text{Mg}_7(\text{SO}_4)_{13}\cdot 15\text{H}_2\text{O}$ ). Salt mineralogy was not the aspect of the  
2 present study. However, this subject needs detailed investigation.  
3 The presence of ferric sulfates (jarosite) in the subsoil considered  
4 to be a potential source of sulfate which is capable of adding new  
5 sulfate salts to the soil. Presently the outcrops of the shale along  
6 the valleys and hillsides in the study area are generating additional  
7 new sulfate salts in Saskatchewan.

#### 8 Oxidation Zone

9           The presence of jarosite and ferric oxides in a 4-5m thick  
10 oxidation zone suggested that this layer was exposed to the atmosphere  
11 prior to the glaciation of the area. Most of the oxidation might have  
12 taken place during the last interglacial period. Van Breeman (1982)  
13 suggested that most of the iron from the oxidation of pyrite ends up  
14 in iron oxides (hematite, goethite). Analyses indicated that there is  
15 a concentration of free iron (CDB-Fe) in the oxidized zone in the  
16 Profile 2 (Table 3). Free iron oxides in the oxidized Cretaceous  
17 marine clay is considered to be the end product of pyrite oxidation.  
18 Extremely low CDB-Fe below 700 cm is a good indication that there is  
19 almost no oxidation in the pyrite containing zone. Several evidences  
20 of this process can be found in Saskatchewan soils. High amounts of  
21 silicate iron in the lacustrine clay materials in comparison with iron  
22 in the Cretaceous marine shales in Saskatchewan were attributed by  
23 Mermut et al. (1984) to the substitution of iron from oxides with  
24 silicate magnesium. Furthermore, the old floral till in Saskatchewan  
25 is known for its red yellow color due to staining by iron oxides. The

1 source of the iron oxides in floral till until today is unknown. It  
2 seems now possible to hypothesize that the red staining in this old  
3 till is due to iron oxides resulted from sulfide oxidation which  
4 remains to be further investigated.

#### 5 Solonetzic Soils

6 Major soils in the area studied are Solonetzic, however  
7 saline soils are found as patches in the depressional areas. Land-  
8 scape analysis and chemistry and mineralogy of salt suggest that  
9 saline soils (Solonchaks) and Solonetzic soils in Saskatchewan owe  
10 their presence in great extent to the sulfide oxidation process. Most  
11 of the Solonetzic soils in the province were likely once saline and  
12 they have acquired Solonetzic characteristics when the salts moved to  
13 lower landscape or transported elsewhere. The presence of Solonetzic  
14 soils next to the saline soils around many lakes in Saskatchewan  
15 confirms this association.

16 The Cedaux soils have high amounts of Na in exchangeable  
17 sites and has Solonetzic features. Under such conditions formation of  
18 Solonetzic soil is almost certain after the desalinization of the top-  
19 soil. We found more evidence of Solonetzic soil formation in areas  
20 where the till mantle is shallow. More field and laboratory studies  
21 are needed to establish this relationship.



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Table 1. pH, EC and ionic composition from the saturation paste of the two Cedaux Profiles.

Depth cm	pH	EC dSm <sup>-1</sup>	K+	Na+	Ca <sup>2+</sup>	Mg <sup>2+</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>
			----- meq/L -----						
Cedaux Profile 1									
0-20	7.8	1.2	0.43	6.00	3.49	1.48	3.54	0.42	<0.10
20-40	8.3	4.8	0.15	40.45	6.99	4.61	40.82	1.52	"
40-80	8.6	17.0	0.28	178.34	15.97	32.92	183.88	3.38	"
80-120	8.2	18.2	0.36	204.44	1.60	34.56	239.50	3.13	"
120-170	5.6	12.9	0.56	134.84	1.70	18.10	143.28	2.45	"
170-220	4.5	10.7	0.77	102.65	1.30	13.17	113.50	2.17	"
220-280	4.3	10.2	0.79	99.17	1.00	13.66	109.34	1.97	"
Cedaux Profile 2									
0-10	7.3	1.3	1.30	2.45	10.58	5.26	5.83	1.41	5.93
100-125	4.9	10.2	0.29	90.32	37.52	60.07	191.04	1.46	<0.10
150-175	4.5	10.0	0.39	91.32	37.32	55.81	194.40	1.69	"
175-200	4.4	8.9	0.37	82.02	32.53	45.71	169.40	1.41	"
225-250	4.5	7.7	0.31	73.43	21.36	32.96	142.68	1.38	"
250-300	4.2	6.1	0.31	55.63	11.78	24.30	102.75	1.27	"
350-400	4.3	6.2	0.40	57.81	11.08	19.34	104.20	1.13	"
400-450	4.6	5.1	0.32	47.33	9.44	12.74	83.31	0.70	"
450-500	4.5	6.1	0.54	63.16	25.32	24.18	126.66	0.82	"
500-550	4.8	5.1	0.28	47.56	10.52	13.19	83.31	0.70	"
550-600	5.5	6.3	0.87	53.46	29.60	21.52	111.08	0.65	0.11
600-700	6.1	3.9	0.22	35.27	4.44	6.00	58.32	0.62	0.21
700-750	8.7	10.9	0.86	117.38	45.30	23.28	212.38	1.69	1.40
750-800	9.0	4.4	0.30	44.22	5.18	3.62	63.88	0.84	1.17

Table 2. Anion distribution in the Cedaux Profile 2 expressed as percent of the total ion in each horizon.

Depth cm	K <sup>+</sup>	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>
0-10	6.6	12.5	54.0	26.9	44.3	10.7	45.0
100-125	0.2	48.0	19.9	31.9	99.2	0.8	<0.1
125-175	0.2	49.4	20.2	30.2	99.1	0.9	<0.1
175-200	0.2	51.1	20.2	28.5	99.1	0.9	<0.1
225-250	0.2	57.4	16.7	25.7	99.0	1.0	<0.1
250-300	0.3	60.5	12.8	26.4	98.7	1.2	0.1
350-400	0.5	65.2	12.5	21.8	98.8	1.1	0.1
400-450	0.5	67.8	13.5	18.2	99.1	0.8	0.1
450-500	0.5	55.8	22.4	21.4	99.3	0.6	0.1
500-550	0.4	66.5	14.7	18.4	99.1	0.8	0.1
550-600	0.8	50.7	28.1	20.4	99.3	0.6	0.1
600-700	0.5	76.8	9.7	13.0	98.6	1.1	0.3
700-750	0.5	62.8	24.3	12.4	98.6	0.8	0.6
750-800	0.6	82.9	9.7	6.8	96.9	1.3	1.8

Table 3. Exchangeable cations (percent of the total exchangeable cations) and free iron (CDB-Fe) in the selected horizons of the Cedaux Profile 2.

<u>Depth</u>	K	Na	Ca	Mg	H	CDB-Fe %
0-10	6.7	0.3	73.7	19.2	0.1	0.72
100-125	2.0	10.3	46.9	40.4	0.4	1.23
175-200	2.5	14.2	29.7	39.0	14.6	1.87
225-250	2.5	21.8	15.1	36.9	23.7	1.32
350-400	2.3	13.5	33.2	31.0	20.0	1.25
500-550	2.9	34.2	17.7	35.9	9.3	0.97
600-700	3.2	21.3	40.4	33.5	1.6	0.73
750-800	3.7	30.5	41.6	21.5	2.7	0.25

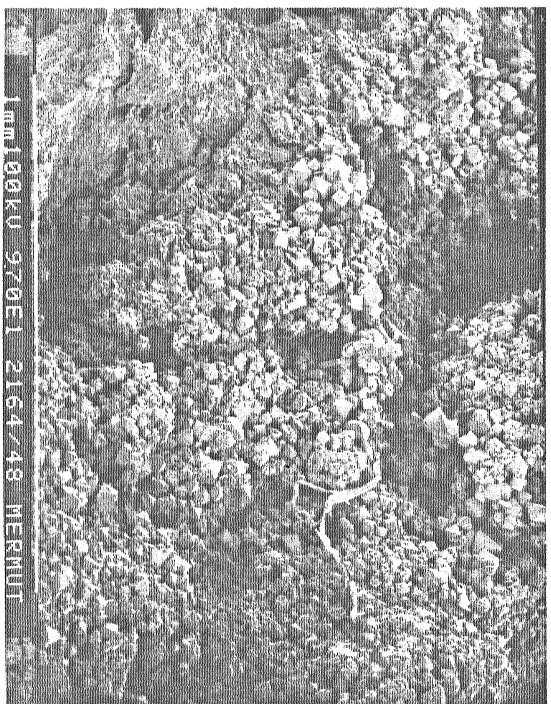


Fig. 1

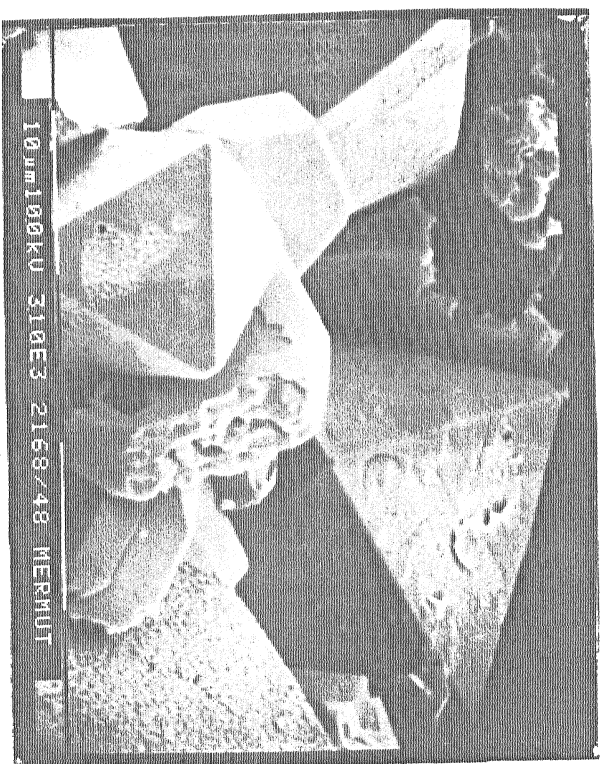


Fig. 2

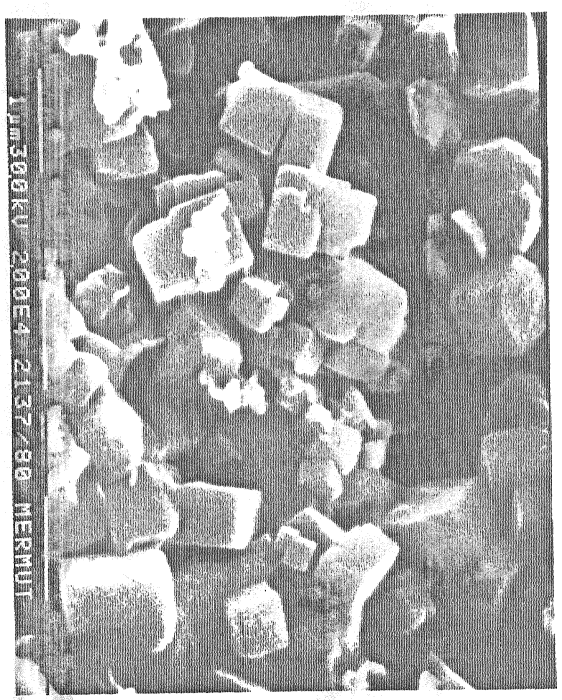


Fig. 3

#### FIGURE CAPTIONS

- Fig. 1 SEM micrograph of perfect octahedral pyrite crystals together with crystals under dissolution process from the reduced zone of Profile 1.
- Fig. 2. SEM micrograph indicating the surface dissolution of large pyrite crystals from the reduction zone of Profile 1.
- Fig. 3. SEM micrograph of Jarosite crystals from the oxidized zone of Profile 1.