

# WEATHERING CHARACTERISTICS OF SALINE AND SODIC MINESOILS IN THE SOUTHWESTERN UNITED STATES<sup>1</sup>

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**Abstract:** Relationships between electrical conductivity (EC) and sodium adsorption ratio (SAR) in reconstructed soils at surface coal mining operations are poorly documented in the literature. Research has focused primarily on agricultural and range soils. Chemical and physical properties of reconstructed soils are unique and quite different from natural soils formed over hundreds of years through pedogenic processes. These differences largely occur because relatively unweathered overburden is exposed during mining processes and subsequently used as a lower root-zone medium (minesoil) during soil reconstruction. Some of these materials are classified as sodic and therefore are considered unsuitable rooting media for establishment of native vegetation. Weatherable minerals (i.e., pyrite, calcite, gypsum, and other geologic substrates) present in minesoils can effectively remediate or mitigate an elevated SAR condition by maintaining EC levels in the soil solution to promote clay particle stability and by providing sources of exchangeable calcium and magnesium. Coversoil (e.g., topsoil) enhances remediation through physical and chemical buffering between sodic root-zone material and the reconstructed soil surface. A laboratory core-study was used to evaluate weathering potential of 10 minesoil materials from three mining operations in the Southwestern United States. Cores were prepared with 15 cm of coversoil over 30 cm of minesoil and subjected to simulated precipitation. Chemical evaluations of weathered materials show significant reductions in EC and SAR and overall improvement of minesoil quality. Chemistry of drainage water from three coversoils shows these materials behave as a chemical buffer above the underlying sodic materials. Coversoils provide a source of calcium and other electrolytes that promote physical stability and enhance remediation of sodic minesoil materials.

Additional Key Words: Sodium adsorption ratio, salinity, minesoils, root-zone material, and weathering

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<sup>1</sup>Paper was presented at the 2005 National Meeting of the American Society of Mining and Reclamation, Breckinridge, CO, June 19-24, 2005. Published by ASMR, 3134 Montavesta Rd. Lexington, KY 40502

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Proceedings America Society of Mining and Reclamation, 2005 pp 765-778  
DOI: 10.21000/JASMR05010765

<https://doi.org/10.21000/JASMR05010765>

## Introduction

Suitability of saline and sodic minesoil materials (e.g. backfill or spoil) used for soil reconstruction at coal mining operations in the Southwestern U.S. has received little focus from the scientific community. In addition, minimal data are available on the effect of coversoils (e.g., topsoil) on minesoil chemistry. The purpose of this research project is to study the chemistry of coversoil and minesoil materials and to provide guidance for the development of appropriate sodium adsorption ratio (SAR) standards at Southwestern U.S. mining operations. The information provided in this paper represents the results of laboratory studies associated with the overall project. Field studies related to this research project will be presented at a future meeting.

Minesoil materials derived from overburden at mining operations in the Southwest are often enriched in sodium ( $\text{Na}^{+1}$ ) as compared to other dominant exchangeable cations (e.g., calcium ( $\text{Ca}^{+2}$ ) and magnesium ( $\text{Mg}^{+2}$ )). Consequently, these materials are classified as sodic or having high SAR values. Although SAR is widely used to evaluate suitability of minesoils, the chemistry of these  $\text{Na}^{+1}$  enriched systems and the effects of coversoil placed over sodic root-zone materials is not well understood or documented. The SAR suitability criteria used for minesoil reconstruction were largely developed from Agricultural Handbook No. 60 (USDA, 1954). It is now known that the findings of this document are flawed because soil electrolyte concentration (e.g., electrical conductivity (EC)) and clay mineralogy were not fully considered in the evaluation of sodic materials (Sumner et al., 1998 and Quirk, 2001). Consequently, the coal mining industry is expending considerable resources to mitigate (often by burial) materials that should not be classified as unsuitable with regard to SAR. Unnecessary mitigation dramatically increases reclamation costs, which are passed to coal consumers.

The chemical and physical properties of minesoils are unique and quite different from natural soils formed through pedogenic processes. This difference largely results from the use of relatively unweathered overburden and interburden as root-zone medium. Although these materials are often classified as sodic ( $\text{SAR} > 13$ ), they typically contain sufficient EC levels to maintain clay flocculation and hence permeability.

$$\text{SAR} = \frac{[\text{Na}^{+1}]}{([\text{Ca}^{+2}] + [\text{Mg}^{+2}])^{0.5}}, \text{ using millimolar concentrations}$$

Weatherable minerals (i.e., pyrite, calcite, and gypsum) are present that can effectively remediate or mitigate an elevated SAR condition by increasing EC in the soil solution and availability of exchangeable cations such as  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$ . Coversoil is placed over root-zone materials during soil reconstruction to enhance revegetation efforts and to provide a physical and chemical buffer between sodic minesoils and the reconstructed soil surface. Coversoils derived from Aridisols and Alfisols often contain calcite ( $\text{CaCO}_3$ ), gypsum ( $\text{CaSO}_4$ ), and other weatherable minerals that provide salts and  $\text{Ca}^{+2}$  to the soil solution.

Development of poor physical conditions including reduced hydraulic conductivity (K) and aeration is the fundamental problem associated with sodic soils. Decline in physical stability and specific ion toxicity can reduce vegetation productivity. The effect of exchangeable sodium percentage (ESP), often estimated using SAR, on soil physical properties is greatly dependent on EC of the soil solution. It is impossible to estimate the impacts of SAR on the physical state of a

soil material without knowing EC of the system (Shanmuganathan and Oades, 1983; Sumner et al., 1998). Any attempt to set critical ESP or SAR values for land management would be arbitrary unless EC levels are taken into consideration simultaneously (Sumner et al., 1998). Research has shown that high SAR values do not cause physical degradation of soil if the system also contains high levels of salts (Quirk and Schofield, 1955; McNeal et al., 1968; Frenkel et al., 1978; Shainberg et al., 1981a; Abu-Sharar et al., 1987; Chiang et al., 1987; Lima et al., 1990; Malik et al., 1992; Curtin et al., 1994; Mace and Amrhein, 2001). In general, the potential for aggregate slaking, soil swelling, and clay dispersion is amplified as ESP increases and EC decreases.

The presence of relatively soluble minerals such as gypsum and calcite can provide significant quantities of electrolytes containing  $\text{Ca}^{+2}$  to the solution. Consequently, gypsum is commonly used as an amendment for reclamation of sodic soils. Ayers and Westcott (1989) interpret sodicity hazard by the occurrence of gypsum. Sodic soils with solid phase gypsum are considered to be self-reclaiming since they provide a long-term slow release supply of  $\text{Ca}^{+2}$ . These soils will typically have  $\text{Ca}^{+2}$  concentrations of about 20 to 30 meq  $\text{L}^{-1}$  and pH levels greater than about 7.0 (Munk, 1996). Over time in many relatively unweathered soils, such as reclaimed coversoil-minesoil pedons, the release of  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  upon physical and chemical weathering will reduce the SAR and lessen Na hazard (Dollhopf, et al., 1980; Carlstrom et al., 1987; USDA, 1993; Munk, 1996; P&M, 1996). Elemental sulfur and  $\text{H}_2\text{SO}_4$  are commonly used in reclamation of sodic soils containing calcite. The acid dissolves calcite, which increases EC and provides  $\text{Ca}^{+2}$  needed to replace  $\text{Na}^{+1}$  on exchange sites. A net downward percolation of water facilitates translocation of  $\text{Na}^{+1}$  displaced from the Ca:Na exchange reaction and remediation of sodic conditions. The fact that minesoils in the Southwest contain gypsum, calcite, and pyrite provides a strong basis for the self-remediation concept. The solubility of gypsum and calcite will contribute electrolytes and  $\text{Ca}^{+2}$  to the solution and pyrite oxidation will enhance dissolution of carbonate minerals (Dubey and Mondal, 1994).

Dollhopf et al. (1980), Jurinak and Wagenet (1982), Richardson and Farmer (1982), and Hall and Berg (1983), investigated natural geochemical weathering effects on sodic overburden and minesoil samples collected from mines in Montana, North Dakota, Colorado, and New Mexico. These laboratory and field studies showed  $\text{Ca}^{+2}$  levels increased during weathering, while significant decreases were recorded for  $\text{Na}^{+1}$ . The importance of mineral weathering can be significant in reducing the sodicity of overburden and minesoil when dealing with slightly weathered calcareous overburden or those that contain predominantly non-swelling kaolinite, illite, and chlorite clay minerals. In two different field studies at the West Decker mine in Montana, SAR levels decreased 8 to 9 units in the upper 30 cm of minesoil over a 2 to 7 year period (Dollhopf et al., 1980 and Richardson and Farmer, 1982). These decreases were apparently due to increases in  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  and leaching of  $\text{Na}^{+1}$  by percolating rainwater and snowmelt water. A portion of the SAR reduction may have been attributable to initial irrigation and amendment use. High EC levels and occasional heavy rain or winter snowmelt promoted downward salt leaching and decreased EC and SAR with time in reclaimed coversoil-minesoil pedons at the San Juan Mine in New Mexico (Carlstrom et al., 1987).

Another important aspect of weathering is associated with the influence of carbon dioxide ( $\text{CO}_2$ ) on calcite solubility. The presence of  $\text{CO}_2$  enhances calcite dissolution (Nadler, et al., 1996). Increased  $\text{CO}_2$  levels from root respiration will increase calcite solubility and increase  $\text{Ca}^{+2}$  in the soil solution. These data support the theory that coversoil and minesoil materials

containing calcite are expected to provide exchangeable  $\text{Ca}^{+2}$  to enhance remediation of sodic conditions.

Tejedor et al. (2003) showed that saline/sodic soils covered by 10 to 15 cm of tephra mulch (basaltic volcanic material), resulted in significant remediation of underlying soils with respect to EC and ESP. After a period of time, unmulched soils maintained their previous character and were extremely saline-sodic (EC of saturation extract ( $\text{EC}_e$ ) = 43 dS m<sup>-1</sup>, ESP = 44), whereas the mulched soils were neither saline nor sodic ( $\text{EC}_e$  = 1.5 dS m<sup>-1</sup>, ESP = 9). The reduction in salinity and sodicity in mulched soils was related to the change in soil moisture regime caused by mulch covering, which increased infiltration and reduced evaporation. The authors attributed remediation to the greater dilution of soil solution through increased soil water content, increased  $\text{Na}^{+1}$  leaching, and dissolution of Ca salts. Coarse-textured coversoils are expected to have a similar mulching affect when applied to saline and sodic minesoils.

As noted previously, the purpose of this research project is to develop an understanding of the chemistry associated with coversoil and minesoil materials at mine sites located in arid and semi-arid regions in the Southwestern U.S. The information generated will be used with data from future field studies to provide guidance for the development of appropriate SAR standards at mining operations in the Southwest.

### **Materials and Methods**

Surface coal-mining operations in the Four Corners region of New Mexico and Arizona were selected as sources of minesoil and coversoil materials. Federal and State regulatory agencies require operators of surface coal mines to regularly conduct monitoring of minesoil materials, prior to reclamation, to determine compliance with site-specific suitability standards. Monitoring results from a total of 51 locations from three mining operations were grouped by EC and SAR and placed into an EC-SAR class (Table 1). The 51 locations represent sites that were sampled and analyzed no more than six months prior to initiation of this study. One monitoring location within each EC-SAR class was selected at random for detailed sampling and analysis. A test-pit was excavated at each selected location (10) and minesoil material was collected from a 1 m horizontal plane to a depth of 90 cm. Sufficient material was passed through a 6.35 mm (0.25 in) sieve to yield approximately 90 kg. Coversoil was collected in equal volumes from a minimum of two stockpile locations at each mine to yield approximately 45 kg.

Sub-samples of homogenized minesoil and coversoil materials were analyzed to establish baseline chemistry and to verify EC and SAR class. Minesoil samples were disaggregated (<2 mm) and coversoils were passed through a #10 sieve (<2 mm). Saturated paste extracts were prepared from subsamples and analyzed for pH, EC, percent saturation, soluble  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Na}^{+1}$ , sulfate ( $\text{SO}_4^{-2}$ ), and SAR. Analysis of pyritic sulfur, percent  $\text{CaCO}_3$ , gypsum, and textural class with percent sand, silt, and clay were also completed.

Cores were constructed in a 55 cm long section of PVC pipe with a 10 cm inside diameter. A PVC cap with a 1.3 cm drain outlet was glued on one end of the PVC pipe and a 20-mesh screen was placed in the bottom of the cap. Washed silica sand (10-20 mesh) was added and compacted to the top of the PVC cap to produce a solid base for the soil core. An additional 20-mesh screen was placed on top of the silica sand to reduce soil particle migration.

Table 1. EC-SAR class and alphabetic class designation for root-zone materials.

Class Reference	EC dS m <sup>-1</sup>	SAR
*	Coversoil	Coversoil
A	0-4	15-25
B	0-4	25-40
C	0-4	>40
D	4-8	<15
E	4-8	15-25
F	4-8	25-40
G	4-8	>40
H	8-18	15-25
I	8-18	25-40
J	8-18	>40

There were two types of cores prepared for this study: 1) coversoil and 2) coversoil over minesoil. Coversoil cores were constructed in triplicate using coversoil materials (N-1, S-1, and K-1) from the three mine operations (9 cores). Coversoil over minesoil cores were constructed in triplicate using each of the 10 minesoils (30 cores) and the randomly selected N-1 coversoil type. All materials were equilibrated with deionized water at a gravimetric moisture content of 0.10 cm cm<sup>-1</sup> to facilitate packing. Cores prepared entirely with coversoil were packed in two 7.5 cm lifts at a density of 1.4 g cm<sup>-3</sup>. Coversoil over minesoil cores were also packed at a density of 1.4 g cm<sup>-3</sup> in two, 15 cm lifts of minesoil followed by two, 7.5 cm lifts of coversoil. The surface was scarified between lifts to minimize variation in bulk density.

Simulation of weathering conditions was developed based on irrigation schedules and/or natural precipitation at the three mine operations. Laboratory tap water was applied to cores at a rate of 2.9 cm over a four-hour period. Tap water chemistry is provided in Table 2. Applications were repeated every fourth day for 28 days with cores being covered between irrigation treatments. Total irrigation was 23.2 cm of water. Effluent from coversoil cores was collected after each irrigation and analyzed for pH, EC, Ca<sup>+2</sup>, Mg<sup>+2</sup>, Na<sup>+1</sup>, and SAR. Cores were disassembled and sampled after the final irrigation application and subsidence of drainage. Coversoil cores were sampled in one 15 cm increment. Coversoil and minesoil material cores were sampled in increments of 0 to 15 cm (coversoil), 0 to 5, 5 to 10, 10 to 20, and 20 to 30 cm (minesoil). Samples were air-dried, disaggregated (<2.0 mm), and analyzed for pH, EC, Ca<sup>+2</sup>, Mg<sup>+2</sup>, Na<sup>+1</sup>, SAR, and SO<sub>4</sub><sup>-2</sup> using the saturated paste extract procedure.

Mean levels of pH, EC, Ca<sup>+2</sup>, Mg<sup>+2</sup>, Na<sup>+1</sup>, SAR, and SO<sub>4</sub><sup>-2</sup> in the 0 to 5, 5 to 10, 10 to 20, and 20 to 30 cm increments of coversoil and minesoil were compared to baseline levels. Subtracting end of experiment values from baseline reference values allowed statistical analysis of materials subjected to simulated weathering. Finally, these differences were averaged over the replications and tested for a significant departure from zero ( $\alpha= 0.05$ ) using a t-test. Mean separations were also conducted among the depth increments separately for each minesoil using Fisher's protected LSD.

## **Results**

EC-SAR classes and letter designation for classes of materials used for this study are provided in Table 1. Analyses of minesoil materials show that seven out of ten classes were represented. Therefore, three of the EC-SAR class treatments were replicated (Table 2).

Table 2. Baseline EC-SAR class, pH, EC, saturation %, SAR, soluble cations, soluble anions, CaCO<sub>3</sub> %, gypsum, and texture of coversoil and minesoil materials.<sup>†</sup>

Material	EC-SAR	pH	EC	Saturation	SAR	Ca	Mg	Na	SO4	CaCO <sub>3</sub>	Gypsum	Clay	Texture
	Class	s.u.	dS m <sup>-1</sup>	%	meq L <sup>-1</sup>	meq L <sup>-1</sup>	meq L <sup>-1</sup>	meq L <sup>-1</sup>	%	g kg <sup>-1</sup>	%		
Tap H <sub>2</sub> O	-	7.65	0.32	-	0.25	1.25	1.52	0.29	0.5	-	-	-	-
N-1 <sup>‡</sup>	-	7.55	4.17	29.9	7.60	19.0	2.80	25.0	43.5	1.9	0.5	12.5	SL
K-1	-	7.8	1.25	36.4	3.00	4.01	2.56	5.4	6.1	3.3	<0.1	20.0	L
S-1	-	7.6	7.60	35.1	10.6	28.4	13.1	48.4	81.7	4.6	2.5	20.0	L
1	B	8.74	2.70	113	39.4	0.50	0.25	24.1	21.1	4.3	1.4	27.5	CL
2	D	8.21	7.44	45.1	12.4	20.0	17.6	53.9	100	1.7	1.5	25.0	L
3	D	8.09	7.87	59.3	13.2	19.6	18.6	57.6	107	3.1	5.7	30.0	CL
4	E	8.47	4.88	40.2	19.6	4.88	4.42	42.2	52.5	1.7	0.3	20.0	L
5	E	7.72	6.12	47.3	18.1	19.0	19.7	79.4	135	0.6	1.8	27.5	CL
6	F	8.32	7.42	44.9	32.3	5.49	4.04	70.6	84.9	0.6	0.5	23.8	SiL
7	G	8.56	4.93	104	49.4	1.23	0.70	48.5	49.7	6.5	1.6	32.5	SiCL
8	I	8.28	11.0	83.6	31.5	17.3	4.55	104	141	4.8	2.8	33.8	CL
9	I	8.44	15.0	65.5	35.3	21.0	13.8	147	201	1.7	12.4	35.0	CL
10	J	8.31	17.0	48.9	50.5	25.7	3.47	193	230	2.0	19.4	30.0	SiCL

<sup>†</sup> EC-SAR class not determined for coversoil materials.

<sup>‡</sup> N-1 was the coversoil type used on all minesoil treatments.

### Minesoils

Irrigation rates closely followed those often used at Southwestern mining operations and provided accelerated weathering conditions expected from natural precipitation over extended periods of time. Cores prepared with minesoils 1, 7, 8, and 9 received irrigations of 11.6, 14.5, 20.3, and 18.9 cm, respectively, because of slow infiltration rates. Shale and siltstone derived minesoils commonly have saturated hydraulic conductivities (K) between  $1 \times 10^{-5}$  and  $1 \times 10^{-6}$  cm sec<sup>-1</sup>. The K of a material is greatly influenced by porosity and pore geometry. Swelling processes change macro-pore geometry, thus compressing pore radii and reducing K. Swelling pressure is amplified in confined systems including rigid wall cores. Saturation percentage of materials 1, 7, 8, and 9 was 113, 104, 83.6, and 65.5%, respectively. Elevated saturation percentage in materials 1, 7, and 8 indicate a predominance of smectitic clays that would swell upon hydration, thus reducing effective porosity and K. Minesoil 9 had the highest clay content (35%) of all samples, which provides a reasonable explanation for low K. Saturation percentage of the minesoils was less than 60% suggesting mixed clay mineralogy. A discussion of weathering trajectories based on comparisons between sample depths and baseline levels (Table 3) for each material follows:

Minesoil 1. Baseline EC and SAR were 2.7 dS m<sup>-1</sup> and 39.4, respectively. Minesoil 1 is largely classified as unsuitable (i.e., exceeding common regulatory standards) with regard to SAR. Core triplicates received 50% of the irrigation treatment because of low K. Saturation percentage was 113% indicating predominance of smectitic type clays. The pH of Minesoil 1 was significantly less than baseline levels at all depths. The pH, EC, Ca<sup>+2</sup>, Mg<sup>+2</sup>, Na<sup>+1</sup>, and SO<sub>4</sub><sup>-2</sup>, levels in coversoil and Minesoil 1 are statistically similar. SAR of Minesoil 1 was higher at all depths than coversoil; however, weathering resulted in a 14-unit decrease in the 0 to 5 cm increment. Mean SAR below 5 cm was approximately 9 units lower than baseline showing moderate improvement in material quality.

Minesoil 2. Baseline EC and SAR were 7.44 dS m<sup>-1</sup> and 12.4, respectively. Minesoil 2 is considered suitable with respect to EC and SAR. The pH of Minesoil 2 was the same as coversoil and significantly lower than baseline levels at all depths. Electrical conductivity of the 0 to 5 cm increment was the same as coversoil and statistically lower than baseline. Non-significant EC decreases were apparent in the 5 to 10 cm and 10 to 20 cm increments. Similarly, Ca<sup>+2</sup>, Mg<sup>+2</sup>, Na<sup>+1</sup>, and SO<sub>4</sub><sup>-2</sup> levels in coversoil and 0 to 5 cm increment were statistically similar. SAR in the upper 10 cm was also statistically similar to coversoil values and 5 to 7 units less than baseline.

Minesoil 3. Baseline EC and SAR were 7.87 dS m<sup>-1</sup> and 13.2, respectively. Minesoil 3 is suitable with respect to EC and SAR. The pH follows a reduction pattern similar to the above materials. Electrical conductivity and Mg<sup>+2</sup> were depleted in the 0 to 5 cm increment, remained unchanged in the 5 to 10 cm increment, and accumulated below 10 cm. Calcium increased at all depths due to apparent dissolution of gypsum and calcite. Dissolution of soluble minerals evidently contributed to the relatively high EC levels that were observed below 20 cm. Calcium levels follow those described by Munk (1996) for gypsum containing soils. Sodium and SO<sub>4</sub><sup>-2</sup> were depleted to a depth of 20 cm and accumulated in the 20 to 30 cm zone. SAR was significantly reduced (6 to 11 units) to levels similar to coversoil in the upper 20 cm and was slightly increased in the 20 to 30 cm zone. Reduction of pH from a moderately alkaline to a neutral condition in this same zone would enhance solubility of carbonate minerals.

Minesoil 4. Baseline EC and SAR were 4.88 dS m<sup>-1</sup> and 19.6, respectively. Minesoil 4 is considered marginally suitable with respect to SAR. The pH of Minesoil 4 unexpectedly increased above baseline levels in the upper 10 cm. The pH at lower depths also showed slight non-significant increases. Electrical conductivity, Ca<sup>+2</sup>, Mg<sup>+2</sup>, Na<sup>+1</sup>, and SO<sub>4</sub><sup>-2</sup> were significantly depleted at all depths and were similar to coversoil levels. SAR in the 0 to 5 cm depth was lower than baseline and was not affected at lower depths. Therefore, reduction of soluble ions was proportionate below 5 cm.

Minesoil 5. Baseline EC and SAR were 6.12 dS m<sup>-1</sup> and 18.1, respectively. Minesoil 5 is considered to be marginally suitable with respect to SAR. The pH was reduced from a slightly alkaline to a slightly acid condition due to apparent pyrite oxidation. Electrical conductivity was slightly reduced in the upper 10 cm and increased in the lower 20 cm. Calcium and Mg<sup>+2</sup> followed a similar pattern as EC. Sodium and SO<sub>4</sub><sup>-2</sup> were significantly reduced in the 0 to 30 cm zone with SAR levels decreasing by 6 to 15 units. The EC and Ca<sup>+2</sup> increases with depth are similar to Minesoil 3 and result from the apparent dissolution of gypsum and calcite.

Table 3. Mean pH, EC, Ca, Mg, Na, SAR, and SO<sub>4</sub>, levels by depth for minesoils 1-10.<sup>†</sup>

Mean pH (s.u.)										
Minesoil	1	2	3	4	5	6	7	8	9	10
SAR-EC Class	B	D	D	E	E	F	G	I	I	J
Coversoil	7.80#	7.70	8.25 a#	8.40 #	6.77	7.93	7.90 #	7.87 #	7.80	7.63
0-5	8.20*	7.17*	7.33 ab	8.67*	6.30*	7.50	8.37*	7.87*	7.27*	7.13*
5-10	8.33*	6.97*	7.90 ab	8.93*	6.17*	7.53	8.50	7.90	7.37*	7.23*
10-20	8.23*	6.97*	7.50 ab	8.80	6.07*	7.63	8.33*	7.73*	7.50	7.37*
20-30	8.27*	7.07*	6.73 b	8.80	6.13*	7.57	8.17*	7.83*	7.60	7.50
Baseline <sup>‡</sup>	8.74	8.21	8.09	8.47	7.72	8.32	8.56	8.28	8.44	8.31

  

Mean EC (dS m <sup>-1</sup> )										
Minesoil	1	2	3	4	5	6	7	8	9	10
SAR-EC Class	B	D	D	E	E	F	G	I	I	J
Coversoil	1.90#	0.42 c#	0.95 d	0.41#	1.63 d	0.51#	1.14 b#	0.61 c#	0.87 c#	0.46 d#
0-5	1.91*	1.32 c*	6.75 c*	0.71*	2.74 dc	1.41*	1.45 b*	0.84 c*	5.60 b*	3.42 cd*
5-10	2.46	3.23 bc	7.79 c	0.98*	5.47 bc	1.31*	2.42 b*	2.42 c*	7.87 b*	5.45 c*
10-20	2.83	5.99 ab	11.9 b*	1.04*	8.29 b	1.73*	3.52 b*	6.21 a*	11.2 a*	10.5 b*
20-30	2.84	8.37 a	17.8 a*	1.14*	12.9 a	3.33	7.28 a	8.24 a*	12.3 a*	15.4 a
Baseline <sup>‡</sup>	2.70	7.44	7.87	4.88	6.12	7.42	4.93	11.0	15.0	17.0

  

Mean Ca (meq L <sup>-1</sup> )										
Minesoil	1	2	3	4	5	6	7	8	9	10
SAR-EC Class	B	D	D	E	E	F	G	I	I	J
Coversoil	4.00#	1.70 c#	1.41 d#	1.46#	4.92 c#	1.31#	2.03 #	2.07 b#	3.00 c#	2.67 c#
0-5	0.67	3.10 c*	26.7 ab*	0.59*	5.33 c	0.76*	0.57*	0.97 b*	21.4 a	28.5 a*
5-10	0.77	14.8 b	29.9 a	0.25*	17.8 b	0.56*	0.80	1.97 b*	19.3 ab	25.9 a
10-20	1.00*	21.1 a	22.5 bc*	0.21*	23.5 a*	0.97*	0.87	10.2 a*	18.6 ab	24.0 b*
20-30	0.93*	22.3 a*	20.7 c	0.80*	21.2 ab*	1.15*	3.57*	13.4 a*	17.1 b*	21.8 b
Baseline <sup>‡</sup>	0.50	20.0	19.6	4.88	19.0	5.49	1.23	17.3	21.0	25.7

  

Mean Mg (meq L <sup>-1</sup> )										
Minesoil	1	2	3	4	5	6	7	8	9	10
SAR-EC Class	B	D	D	E	E	F	G	I	I	J
Coversoil	0.70#	0.27 d#	0.67 d	0.36#	1.21 d	0.29#	0.40	0.43 b#	0.60 d	0.50 #
0-5	0.27	1.37 d*	8.22 c*	0.48*	2.04 d*	0.42*	0.20	0.23 b*	5.80 c*	1.73 *
5-10	0.30	9.00 c	18.7 ab	0.34*	7.87 c	0.34*	0.27*	0.53 b*	7.87 bc*	1.70 *
10-20	0.43	15.6 b	17.8 b	0.32*	15.9 b*	0.40*	0.40*	2.40 ab*	9.73 ab*	2.03 *
20-30	0.43	19.5 a	21.0 a*	0.35*	19.0 a	0.76*	1.77	3.70 a*	10.9 a*	2.60 *
Baseline <sup>‡</sup>	0.25	17.6	18.6	4.42	19.7	4.04	0.70	4.55	13.8	3.47

Table 3. Continued.

	Mean Na (meq L <sup>-1</sup> )									
Minesoil	1	2	3	4	5	6	7	8	9	10
SAR-EC Class	B	D	D	E	E	F	G	I	I	J
Coversoil	14.4#	3.27 c#	3.41 c#	2.43#	4.08 c#	3.79 b#	8.43 c#	4.43 c#	5.27 e#	3.10 d#
0-5	17.0*	10.5 c*	7.57 c*	6.74*	6.62 bc*	10.5 b*	13.0 bc*	7.00 c*	40.8 d*	18.0 d*
5-10	21.9	15.7 c*	12.1 c*	9.77*	10.4 bc*	10.7 b*	23.3 bc*	20.3 c*	69.6 c*	49.0 c*
10-20	26.2	39.6 b	33.0 b*	10.3*	22.3 b*	16.5 ab*	28.7 b*	56.8 b*	108 b	103 b*
20-30	25.3	63.4 a	66.2 a*	10.7*	55.6 a*	31.5 a*	73.5 a	81.1 a	130 a	169 a
Baseline <sup>‡</sup>	24.1	53.9	57.6	42.2	79.4	70.6	48.5	104	147	193

  

	Mean SAR									
Minesoil	1	2	3	4	5	6	7	8	9	10
SAR-EC Class	B	D	D	E	E	F	G	I	I	J
Coversoil	9.33 b#	3.30 b#	3.40 b#	2.57 b#	2.37 b#	4.40 c#	7.63 c	3.97 c#	3.93 c#	2.47 d#
0-5	25.7 a*	7.13 b*	1.80 b*	9.43 b*	3.50 b*	13.7 b*	21.30 b*	9.10 c*	10.80 c*	4.63 d*
5-10	30.3 a	5.10 b*	2.43 b*	18.0 a	3.33 b*	16.4 b*	42.3 a	18.0 b*	18.7 b*	13.3 c*
10-20	30.0 a	9.03 ab	7.37 ab*	20.2 a	5.07 ab*	20.9 b	48.0 a	22.7 ab*	28.7 a	28.7 b*
20-30	30.0 a	14.0 a	14.5 a*	18.5 a	12.4 a*	32.1 a	44.7 a	27.7 a	35.0 a	48.0 a*
Baseline <sup>‡</sup>	39.4	12.4	13.2	19.6	18.1	32.3	49.4	31.5	35.3	50.5

  

	Mean Sulfate (meq L <sup>-1</sup> )									
Minesoil	1	2	3	4	5	6	7	8	9	10
SAR-EC Class	B	D	D	E	E	F	G	I	I	J
Coversoil	13.5#	1.63 d#	3.60 d#	0.82 #	8.36 d#	1.99 b#	6.70 c#	2.43 c#	5.83 e#	2.20 e#
0-5	11.6*	6.67 d*	42.2 c*	1.36*	12.3 d*	6.17 b*	7.77 c*	5.17 c*	63.5 d*	36.5 d*
5-10	15.9	34.1 c*	53.5 c*	2.04*	34.5 c*	7.01 b*	15.5 c*	18.2 c*	89.5 c*	54.0 c*
10-20	21.0	64.9 b	75.8 b*	2.55*	62.0 b*	10.4 ab*	37.3 b	63.2 b*	127 b*	109 b*
20-30	19.9	93.6 a	114 a*	3.23*	93.2 a*	24.0 a*	67.4 a	91.4 a*	148 a*	184 a*
Baseline <sup>‡</sup>	21.1	100	107	52.5	135	84.9	49.7	141	201	230

<sup>†</sup> Mean values followed by the same letter are not significantly different at the 0.05 level.

<sup>‡</sup> Baseline levels are provided for minesoils.

# Post treatments levels in N-1 coversoil are significantly different than baseline levels ( $\alpha = 0.05$ ).

\* Post treatment levels in root-zone materials are significantly different than baseline levels ( $\alpha = 0.05$ ).

**Minesoil 6.** Baseline EC and SAR were 7.42 dS m<sup>-1</sup> and 32.3, respectively. Minesoil 6 is marginally unsuitable with respect to SAR. The pH was similar to coversoil at all depths, but was not significantly less than baseline. The EC, Ca<sup>+2</sup>, Mg<sup>+2</sup>, Na<sup>+1</sup>, and SO<sub>4</sub><sup>-2</sup> followed similar trends with significant depletion below baseline levels at all depths. In addition, levels of these parameters were similar to coversoil except Na<sup>+1</sup> and SO<sub>4</sub><sup>-2</sup> at the 20 to 30 cm depth. SAR in the upper 10 cm was significantly reduced by more than 15 units largely improving material quality.

**Minesoil 7.** Baseline EC and SAR were 4.93 dS m<sup>-1</sup> and 49.4, respectively. Minesoil 7 is considered to be unsuitable with respect to SAR. Cores prepared with Minesoil 7 received 62% of the irrigation treatment due to low K. The saturation percentage was 104%, which reduces K as previously described in this section. The pH followed reduction pattern similar to materials previously discussed. Electrical conductivity and Na<sup>+1</sup> followed similar trends with significant depletion in the upper 20 cm. Calcium, Mg<sup>+2</sup>, and SO<sub>4</sub><sup>-2</sup> were also slightly depleted in the same zone. A significant 28-unit reduction in SAR was observed in the 0 to 5 cm increment largely

improving minesoil quality with respect to SAR. Minimal changes in SAR at lower depths were apparently due to reduced leaching from less irrigation.

Minesoil 8. Baseline EC and SAR were 11.0 dS m<sup>-1</sup> and 31.5, respectively. Minesoil 8 is considered to be marginally unsuitable with regard to SAR. Cores prepared with Minesoil 8 received 88% of the irrigation treatment due to low K. Saturation percentage of this material was 84% indicating a moderate shrink-swell potential and smectitic clay component, but to a lesser extent than minesoils 1 and 7. The pH followed a reduction pattern similar to those previously discussed. Electrical conductivity, Ca<sup>+2</sup>, Mg<sup>+2</sup>, and SO<sub>4</sub><sup>-2</sup> were significantly depleted at all depths while Na<sup>+1</sup> and SAR were significantly lower than baseline values in the upper 20 cm. All parameters levels in the 0 to 5 cm increment were statistically the same as coversoil. Root-zone material quality improved in the upper 20 cm as SAR levels decreased by 9 to 22 units.

Minesoil 9. Baseline EC and SAR were 15 dS m<sup>-1</sup> and 35.3, respectively. Minesoil 9 is largely classified as unsuitable with regard to elevated EC and SAR. Cores prepared with Minesoil 9 received 81% of the irrigation treatment. The pH of this material followed a similar reduction pattern as materials discussed above. EC was significantly less than baseline at all depths with a nearly 10 unit reduction in the 0 to 5 cm increment. Calcium was maintained at a level similar to background at all depths due to apparent gypsum dissolution. Sodium was depleted at all depths with significant reductions in the upper 10 cm. SAR followed a similar trend with Na<sup>+1</sup> and was reduced by 17 to 24 units in upper 10 cm, again showing significant improvement in minesoil quality with respect to SAR.

Minesoil 10. Baseline EC and SAR were 17 dS m<sup>-1</sup> and 50.5, respectively. This minesoil is classified unsuitable because of elevated EC and SAR. The pH of Minesoil 10 followed reduction trends similar to other materials discussed above. Electrical conductivity, Na<sup>+1</sup>, and SAR were significantly reduced below baseline levels in the upper 20 cm with Na<sup>+1</sup> being depleted by 90 to 175 meq L<sup>-1</sup>, SAR by 22 to 46 units, and EC by 6.5 to 13.5 dS m<sup>-1</sup>. Material from the upper 20 cm showed significant improvement in minesoil quality with the upper 5 cm becoming a very slightly saline, non-sodic material. In addition, Na<sup>+1</sup> and SAR levels at the same increment were statistically similar to the coversoil. Calcium remained relatively consistent with baseline levels at all depths, due to apparent gypsum dissolution, while Mg<sup>+2</sup> and SO<sub>4</sub><sup>-2</sup> were significantly depleted.

In general, there was a relationship between EC, SAR, and weathering. Class D, E, F, and G minesoils represented EC 4 to 8 dS m<sup>-1</sup> and SAR of < 15, 15 to 25, 25 to 40, and > 40, respectively. Although the data are variable, reduction in SAR was inversely related to SAR level. This is partially due to the reduced irrigation treatment on the class G minesoil. The least amount of weathering with regard to SAR was associated with minesoils that had SAR > 35 and EC < 5.0 dS m<sup>-1</sup>. Materials with high saturation percentage and associated low K values showed the least amount of weathering with regard to SAR level.

The behavior of Ca<sup>+2</sup> in these minesoils was closely related to gypsum content. Calcium levels were static or increased in some portion of the profile for all minesoils, except 8, that contained at least 1.5 g kg<sup>-1</sup> of gypsum. Calcium concentrations were also related to pH where the highest concentrations associated with materials that weathered from alkaline to a slightly alkaline or neutral pH. Thus, gypsum dissolution and apparent pyrite oxidation are important weathering processes related to “self remediation” of minesoils.

### Coversoils

Coversoil cores received the same irrigation treatment as cores prepared with coversoil and minesoil materials. Mean pH, EC,  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Na}^{+1}$ , and SAR of drainage water after each irrigation treatment is provided in Table 4. The initial 2.9 cm irrigation application was stored in the coversoil materials and was not analyzed. Mean concentration of soluble ions and SAR of drainage water were inversely related to irrigation treatment. N-1 was the coversoil used for cores prepared with minesoil materials discussed above. N-1 contains 0.5 g  $\text{kg}^{-1}$  gypsum and 1.9%  $\text{CaCO}_3$ . Drainage from irrigations 2 through 7 applied to N-1 material contains relatively high concentrations of soluble ions. Ion levels in drainage water from the final irrigation approach levels in the lab water used for this study. The S-1 material provides the highest ion levels in drainage water with a predominance of  $\text{Ca}^{+2}$ . Water percolating from S-1 materials is expected to enhance stability of underlying root-zone materials because of EC ( $3.31 \text{ dS m}^{-1}$ ), low SAR (1.13), and high  $\text{Ca}^{+2}$  concentration ( $27.5 \text{ meq L}^{-1}$ ). The high  $\text{Ca}^{+2}$  levels in drainage water from S-1 result from the apparent dissolution of gypsum ( $2.5 \text{ g kg}^{-1}$ ) and calcite (4.6%) contained in the material. Drainage from K-1 materials also contains relatively high concentrations of soluble  $\text{Ca}^{+2}$  that would promote stability and remediation of underlying sodic materials. Calcium levels in K-1 materials are apparently related to calcite solubility since this material does not contain a measurable quantity of gypsum, but contains 3.3%  $\text{CaCO}_3$ .

Table 4. Mean pH, EC, Ca, Mg, Na, and SAR of drainage water from three coversoil materials subsequent to each irrigation treatment.

Irrigation #	Coversoil Material	pH s.u.	EC $\text{dS m}^{-1}$	Ca $\text{meq L}^{-1}$	Mg $\text{meq L}^{-1}$	Na $\text{meq L}^{-1}$	SAR
2	N-1	8.09	6.71	30.5	5.21	49.0	11.6
3	N-1	8.30	4.82	21.9	3.75	35.9	10.0
4	N-1	8.36	2.56	9.92	1.74	17.6	7.31
5	N-1	8.41	2.60	3.07	0.64	9.22	6.77
6	N-1	8.59	0.84	1.62	0.39	6.87	6.84
7	N-1	8.34	1.44	1.16	0.27	5.60	6.62
8	N-1	8.42	0.60	0.90	0.21	5.00	6.70
2	S-1	8.06	9.52	28.2	16.2	70.5	15.0
3	S-1	8.28	7.56	23.1	13.2	59.5	14.0
4	S-1	8.24	6.27	21.6	11.5	44.6	11.0
5	S-1	8.20	10.78	22.4	11.1	31.0	7.59
6	S-1	8.25	4.10	24.4	11.4	18.9	4.46
7	S-1	8.04	7.24	24.9	11.0	9.8	2.32
8	S-1	8.14	3.31	27.5	11.4	5.01	1.13
2	K-1	8.06	2.39	11.4	6.32	8.49	2.85
3	K-1	8.44	1.11	4.37	2.57	5.29	2.84
4	K-1	8.46	0.80	2.84	1.81	4.20	2.76
5	K-1	8.44	1.44	2.32	1.49	3.69	2.68
6	K-1	8.62	0.65	2.26	1.44	3.45	2.54
7	K-1	8.33	1.28	2.10	1.39	3.15	2.38
8	K-1	8.52	0.58	2.42	1.46	3.18	2.29
Water	-	7.65	0.32	1.25	1.52	0.29	0.25

## **Conclusions**

The overall weathering trajectory of minesoils used in this study is a reduction of soluble cations and anions, primarily  $\text{Na}^{+1}$  and  $\text{SO}_4^{-2}$ , and improvement in quality with regard to EC and SAR. These materials follow an expected weathering sequence where the most soluble ions are translocated from the coversoil/minesoil material contact to lower depths in the profile. Electrical conductivity largely follows the same trajectory as  $\text{Na}^{+1}$  and  $\text{SO}_4^{-2}$ , which are the most mobile ions and largely control EC in these systems. The 0 to 5 cm increment of minesoil is comparable to coversoil chemistry after weathering. Deep leaching events resulting from natural precipitation or irrigation can substantially improve minesoil quality with regard to salinity and sodicity.

Coversoil effluent chemistry supports our hypothesis that these materials provide a chemical buffer between atmospheric water and sodic minesoil materials. Soluble ions translocated from coversoil into minesoils reduce the possibility of aggregate slaking and clay particle dispersion because of increased EC and increased levels of soluble  $\text{Ca}^{+2}$  that will replace  $\text{Na}^{+1}$  on clay particle exchange sites.

Carbonate chemistry plays an important role in the weathering of coversoil and minesoil materials. This study was conducted under laboratory conditions without influences from plants that would be present under field conditions. The  $\text{pCO}_2$  is expected to increase in reconstructed minesoils from root respiration as vegetation is established increasing calcite solubility. Minesoils in this study contain 0.04 to 0.24% pyritic sulfur and 0.64 to 6.5%  $\text{CaCO}_3$  on a mass basis. Chemical and biological oxidation of pyritic sulfur will generate protons in the soil solution and increases calcite solubility resulting in more  $\text{Ca}^{+2}$  available for exchange reactions.

SAR levels were consistently reduced by 23, 15, 10, and 7 units, respectively, for baseline root-zone materials classified as unsuitable, marginally unsuitable, marginally suitable, and suitable. This condition is clearly related to convective  $\text{Na}^{+1}$  leaching; chemistry of the solution percolating through coversoils into minesoil materials; and dissolution of  $\text{Ca}^{+2}$  bearing minerals. Weathering processes will be enhanced under field conditions because of root respiration, increases in organic matter, biochemical reactions, wetting/drying, and freeze/thaw cycles. A field study has been initiated to investigate weathering processes and plant root distributions in saline and sodic minesoils that have been reclaimed for 10 years.

## **Acknowledgments**

The Western Research Institute, Peabody Western Coal Company-Kayenta Mine, BHP-Billiton Navajo Coal Company, and BHP-Billiton San Juan Coal Company provided funding for this project. Thanks are extended to Bob Postle (Office of Surface Mining), Joe Vinson (New Mexico Mining and Minerals Division), and Dr. George Vance (University of Wyoming) for their assistance with development and review of this work.

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