Fine-Grained Mixtures: Fabric Formation and Control

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ABSTRACT: Fabric formation in fine-grained particulate materials depends on pore fluid characteristics and the mineral and geometric characteristics of particles. The behavior of both individual mineral systems and mineral mixtures is studied through macroscale tests involving a wide range of solid volume fractions and strain levels. Results show that (1) a clear fabric map develops on the pH-ionic concentration space for single mineral systems, (2) Coulombic attraction between oppositely charged mineral particles in kaolinite-calcium carbonate mixtures heavily influences particle associations at low solids content, (3) the influence of an anionic polymer on single or mixed mineral systems is surface-charge dependent, (4) the response can be further modified by adding divalent cations to affect the cation-to-polymer ratio and control the level of particle associations within single and mixed mineral systems treated with polymers. These results are relevant to many natural soil environments and the possible development of engineered mineral mixtures for industrial applications.

INTRODUCTION

Fabric formation is the physical manifestation of the interplay between particle geometry and various particle-level forces. Due to their small size and high specific surface, fabric formation in clay-sized particles under low confinement is dominated by interparticle electrical forces rather than by particle self weight, and reflects the prevailing platy particle geometry.

The magnitude of electrical forces, i.e. Coulombic, double layer repulsion, and van der Waals attraction, acting between particles in a polar fluid environment typically depends on the fluid pH and ionic concentration (Santamarina et al. 2002). Palomino and Santamarina (2005), and Wang and Siu (2006) attempt a systematic approach to exploring the effect of pore fluid pH and ionic concentration on fabric formation over a wide range of both pH and ionic concentration.

Particle mixtures often exhibit behavior not present in the individual components and deviate from values predicted by simple mass-average interpolations, for example, when the percolating skeleton changes from clay-controlled to sand-controlled. Most natural soils are particle mixtures. Their mineralogical makeup depends on the source material, depositional environment, and post-depositional chemical reactions. Mineral mixtures are also common in engineering practice; indeed, various soil improvement methods involve mixing powders such as lime or Portland cement into the soil mass.
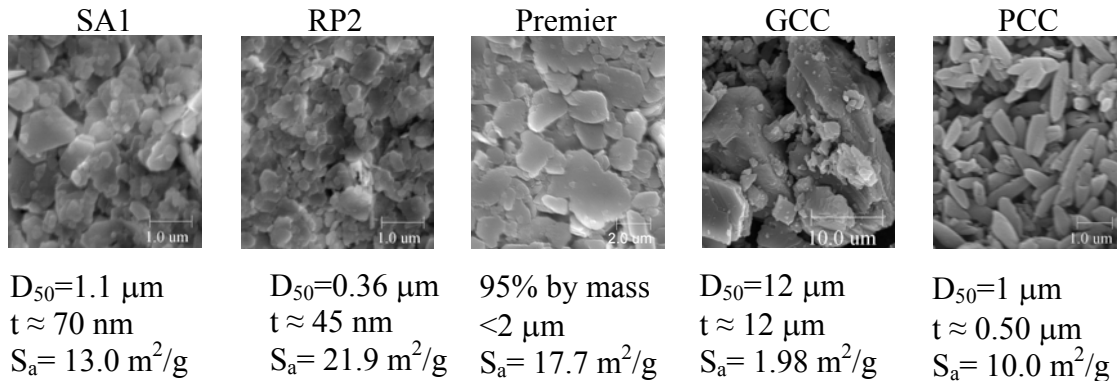
The behavior of fine-grained (D_{50}<~20 μm) mineral mixtures is a complex function of geometric characteristics and electrostatic interactions. For example, the liquid limit of kaolinite and bentonite or bentonite and illite mixtures is a non-linear function of mass fraction of bentonite (Ahmad et al. 2000).

We report herein a study on the behavior of single mineral powders as a function of pH and ionic concentration, mixtures of kaolinite and calcium carbonate, and the alteration of the mineral surface. We select tests that provide information related to fabric formation and granular interactions: sedimentation, viscosity and liquid limit. These macroscale tests cover a wide range of solid concentrations and strain conditions. The goals of this research are to develop a comprehensive understanding of fine particle behavior, its dependence on pore fluid characteristics, and the application of this enhanced understanding to fabric control for the development of engineered fabrics.

MATERIALS

Five mineral powders are studied: three kaolin clays and two types of calcium carbonate. Scanning electron micrographs of the clays and carbonates are presented in Figure 1. The kaolin clay particles are platy (~2-dimensional). The RP2 clay has smaller more randomly-shaped particles compared to the larger, well-crystallized SA1 particles (note the characteristic pseudo-hexagonal shape). The GCC particles are bulkier (3-dimensional) than the kaolin particles, and have irregular surfaces. PCC particles are regular ellipsoids of uniform size, with a ~1.8μm long axis and ~4:1 slenderness.

The mineral surfaces are modified with a commercially available dispersant: sodium polyacrylate (Colloid 211, Rhône-Poulenc, Vinings Industries, Marietta, GA)–specific gravity of 1.30 at 25°C, and molecular weight 3400 g/mol (chains of 34 monomers).

| SA1	RP2	Premier	GCC	PCC
D_{50}=1.1 μm	D_{50}=0.36 μm	95% by mass	D_{50}=12 μm	D_{50}=1 μm
t ≈ 70 nm	t ≈ 45 nm	<2 μm	t ≈ 12 μm	t ≈ 0.50 μm
S_a= 13.0 m²/g	S_a= 21.9 m²/g	S_a= 17.7 m²/g	S_a= 1.98 m²/g	S_a= 10.0 m²/g

FIG. 1. Scanning electron microphotographs of minerals used in this study. Note: D_{50} = average particle diameter, t = particle thickness, S_a = specific surface.

KAOLINITE FABRIC MAP IN THE pH-IONIC CONCENTRATION SPACE

In their simplest form, fabric formation and alteration in clay minerals can be captured in the pH-concentration space. The resulting fabric formation map is different for different clay minerals, and it may also vary with the valence and size of prevailing ions. A summary of postulated particle associations for kaolinite in NaCl electrolytes is shown in Figure 2. This

fabric map is based on published data found in the literature (Brady et al. 1996; Melton and Rand 1977; O'Brien 1971; Rand and Melton 1977; Schofield and Samson 1954; van Olphen 1977).

A modified fabric map based on the sedimentation and rheological parameters for the RP2 kaolinite is shown in Figure 3. This map and observed trends are in general agreement with the major characteristics of the proposed fabric map for kaolinite and NaCl presented in Figure 2, which is derived on conceptual considerations and a synthesis of published results obtained by various authors using different sources of kaolinite.
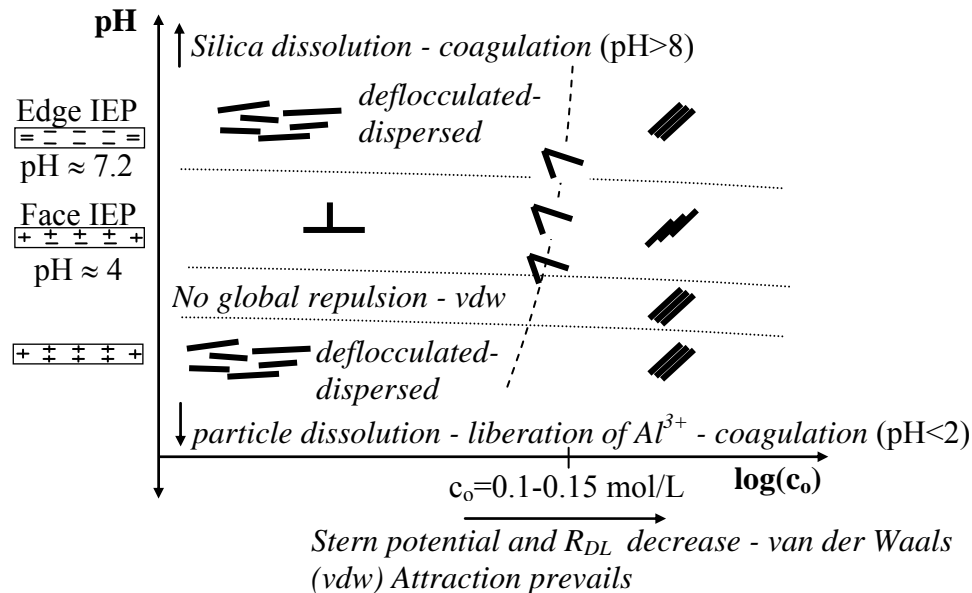
FIG. 2. Hypothesized fabric map for kaolinite in NaCl electrolyte (c_o = concentration) preferred minimum energy configurations (after Santamarina et al. 2002).

KAOLINITE-CARBONATE MIXTURES: GRAIN GEOMETRY AND MINERAL CHEMISTRY

Kaolinite and calcium carbonate represent two very different types of particle and mineral surface charge characteristics. Clay particles are platy, while the carbonate particles are either elongated (PCC) or blocky (GCC). Kaolinite particle faces have a net negative charge, while $CaCO_3$ particles have a net positive charge at neutral pH conditions (Stumm et al. 1992). The zeta potential (electrical potential within the double layer at the slip plane) for both materials varies with pH. Kaolinite zeta potential ranges from positive values at very low pH (~ +5 mV at pH 1.5) to negative values at moderate to high pH (Yuan and Pruett 1998). The isoelectric point of kaolinite typically ranges between 4 and 6 (Drever 1997; Sposito 1989; Yuan and Pruett 1998), while that of $CaCO_3$ is between 8 and 10.5 (Siffert and Fimbel 1984). The significantly different self-buffering pH of the individual minerals implies not only mutual attraction at intermediate pH but also mineral dissolution leading to a different stable pore fluid pH.

Even in the case of fine grains, particle geometry makes an important contribution to overall behavior. Grain size dictates the relative contribution of gravimetric and electrical forces dominating the particle behavior. Figure 4 illustrates probable particle interactions among single minerals and mineral mixtures for both coarse-grained and fine-grained materials. Coarse-
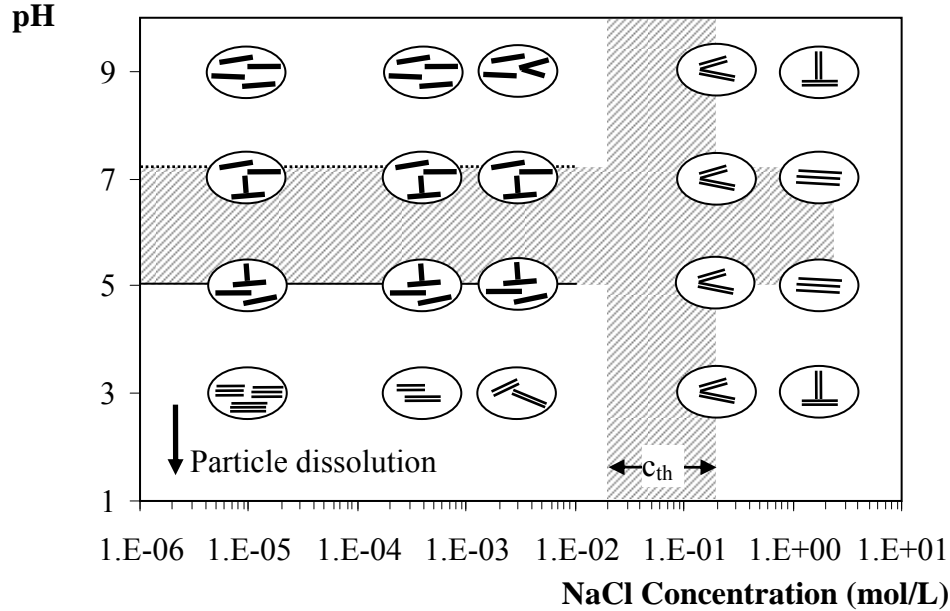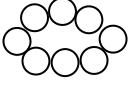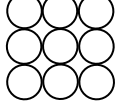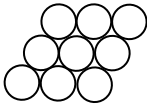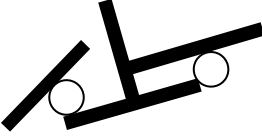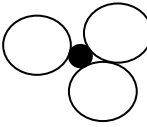
FIG. 3. Kaolinite RP2 fabric map. The shaded areas represent changes in particle association mode due to boundary/transition conditions, and c_{th} is the threshold salt concentration between pH-dependent and independent behavior (Palomino and Santamarina 2005).

grained particle fabric ($D_{50}>\sim 50\mu m$) develops through gravimetric forces. Particle packings include stacked configurations for platy particles, such as mica flakes, and simple cubic and tetrahedral configurations for spherical particles. Mixtures of spherical particles with varying diameters form denser packings than single-sized particles, while platy-spherical mixtures may form more open fabrics due to particle bridging (Lee et al. 2007).

ANIONIC POLYMER INFLUENCE ON SINGLE MINERAL AND MINERAL MIXTURE SYSTEMS

We use the dispersant sodium polyacrylate (NaPAA: $[CH_2CH(COONa)]_n$) to modify and manipulate the apparent mineral surface charge. When the NaPAA molecule is exposed to water, bound sodium ions become hydrated and dissociate from the polymer backbone so that the polymer becomes negatively charged, i.e. anionic. The primary mechanisms for adsorption of NaPAA onto the kaolinite surface are typically thought to be Coulombian attraction between the negative carboxylate groups and the positive edge and basal sites (Diz and Rand 1990; Järnström and Stenius 1990) or hydrogen bonding between the unionized carboxyl groups and the edge oxygens (Michaels and Morelos 1955). In addition to pH, the electrolyte composition has further effects on the NaPAA molecule. In the presence of free Ca^{2+} ions, the polyacrylate molecule adsorbs the divalent cations at the negative carboxylate ion sites. Saturation occurs at some critical ratio of total Ca^{2+} ions to the total number of polyacrylate segments; this ratio approaches 0.3 bound Ca^{2+} ions per polyacrylate monomer at pH=8 (Järnström and Stenius 1990).

	Fine Grained *Electrical Force Control*	Coarse Grained *Gravimetric Force Control*
Single Minerals	Dispersed Flocculated EF Flocculated FF Aggregated	Stacked e.g., crushed mica Loose Dense
Mixtures	Chemistry + Geometry	Geometric effects

FIG. 4. Mixtures in coarse and fine grained soils. Probable particle associations in single mineral and mineral mixture systems.

Single Minerals

Figure 5(a) summarizes the sedimentation heights observed 22 days after the initiation of each test. Sediment becomes more voluminous with flocculation, i.e. higher sediment height, especially for EF flocculated systems; this situation prevails at low ionic concentration near the isoelectric point (Figure 2). Liquid limits for the corresponding cases are shown in Figure 5(b) (fall cone device – BS 1377).

Salient trends include: (1) NaPAA induces dispersion at low and high solids contents for all tested minerals. (2) $CaCl_2$ has some measurable flocculation capability when mixtures include sodium polyacrylate. (3) The level of response to NaPAA and NaPAA with $CaCl_2$ varies for each material and the solids volume fraction, even within the same mineral group. (4) RP2 kaolin is the most sensitive while ground calcium carbonate GCC is the least sensitive material to changes in pore fluid.

Mineral Mixtures

For this part of the study, we utilize a paper coating-quality kaolinite clay pretreated with NaPAA (Premier). The anionic polymer acts as an electrostatic stabilizer by binding to positive surface sites typically found on kaolinite particle edges.

Any exposed negative sites along the polymer chain have the ability to bind to other positive sites such as the surface calcium sites on carbonate particles. Hence, the behavior of the Premier clay is assessed in combination with PCC. Premier clay particles and PCC particles are similar size (Figure 1).
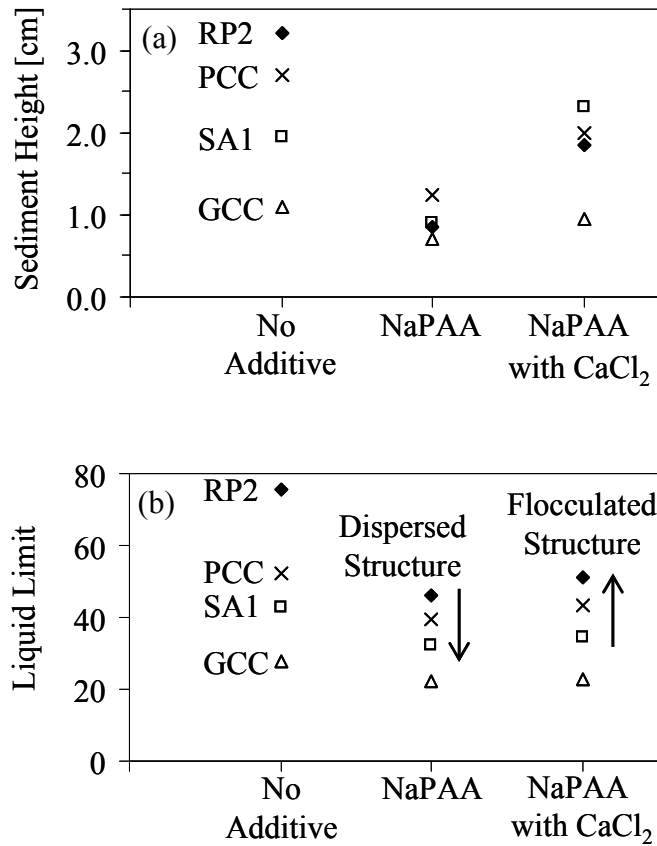
FIG. 5. (a) Suspension sediment heights at 22 days and (b) liquid limits for kaolinite and calcium carbonate mineral grains. Cases: without additives, with sodium polyacrylate, and with sodium polyacrylate plus 0.002 M calcium chloride. Arrows indicate increasing dispersiveness or flocculation.

The sedimentation height of Premier-PCC mixtures is shown in Figure 6. Premier-PCC particle interaction is enhanced through pore fluid modification. $CaCl_2$ is added to the Premier-PCC mixture suspensions. Ca^{2+} ions can bind to the sites vacated by Na^+ along the polyacrylate chain. The excess positive charge promotes flocculation between polymer-coated kaolinite particles. These additional particle interactions manifest as larger sediment heights. Without $CaCl_2$, the maximum sediment height at 23 days occurs for the 25% mass fraction of clay. This maximum sediment height is exceeded by the sediment heights of all mixtures containing $CaCl_2$. Flocculation effects induced by $CaCl_2$ are also observed through viscosity measurements (Palomino 2004).

CONCLUSIONS

This study shows that the behavior of fine-grained materials, both individual mineral powders and mineral mixtures, can be effectively modified and controlled by altering the surface chemistry of minerals, salt type and concentration in the pore fluid, and by introducing materials with differing surface chemistry.
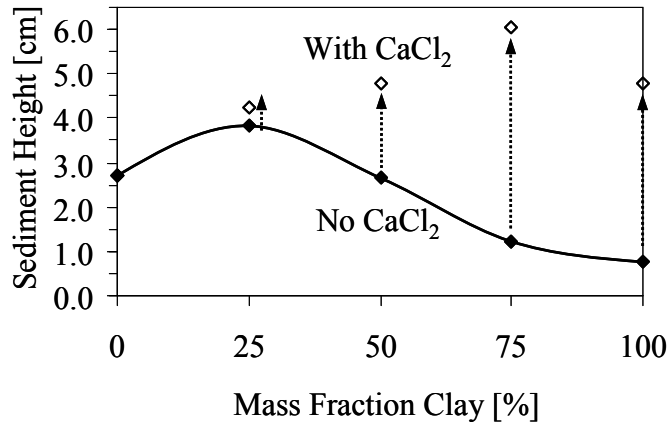
FIG. 6. Controlling particle interaction through changes in surface chemistry and pore fluid. Final sediment height at 23 days for Premier-PCC mixtures with and without CaCl$_2$.

Pore fluid characteristics pH and ionic concentration play a critical role in fabric formation within fine-grained single mineral systems. Coulombic, van der Waals, and double layer repulsion forces can be enhanced or repressed to achieve flocculation or dispersion.

Mixing two minerals with very different surface chemistry creates a greater degree of structure than single mineral systems. Charge and charge site locations influence fabric formation resulting in inter-mineral associations that produce larger flocs or aggregates. Mixtures of kaolinite and calcium carbonate grains exhibit behavior that is related to the pH-dependent mineral surface charge, the relative size and shapes of the particles, and their mass fraction: particle flocculation takes place due to electrostatic interactions between the positively charged calcium carbonate and the negatively charged kaolinite particles at carbonate-controlled pH conditions; fabric is "opened" when large platy clay particles bridge rounded or ellipsoidal-shaped carbonate particles (round cross-section); a high-porosity fabric can be achieved with low percentages of carbonate, and the dependence of sedimentation and viscosity on particle associations gives way to specific surface in high solids content tests, such as the liquid limit.

ACKNOWLEDGMENTS

REFERENCES

Ahmad, N. S., Karunaratne, G. P., Chew, S. H., and Lee, S. L. (2000). "Bentonite-Kaolinite Mix for Barrier Systems." Geo-Denver 2000, T. F. Zimmie, ed., ASCE, Denver, Colorado, 93-104.

Brady, P. V., Cygan, R. T., and Nagy, K. L. (1996). "Molecular Controls on Kaolinite Surface Charge." *J. Colloid Interf. Sci.*, 183(2), 356-364.

Diz, H. M. M., and Rand, B. (1990). "The Mechanism of Deflocculation of Kaolinite by Polyanions." *Brit. Ceram. Trans. J.*, 88, 77-82.

Drever, J. I. (1997). *The Geochemistry of Natural Waters : Surface and Groundwater Environments*, Prentice Hall, Upper Saddle River, N.J.

Järnström, L., and Stenius, P. (1990). "Adsorption of Polyacrylate and Carboxy Methyl Cellulose

on Kaolinite: Salt Effects and Competitive Adsorption." *Colloid. Surface.*, 50, 47-73.

Lee, J. S., Guimaraes, M., and Santamarina, J. C. (2007). "Micaceous Sands: Microscale Mechanisms and Macroscale Response." *J. Geotech. Geoenviron. Eng.*, in print.

Melton, I. E., and Rand, B. (1977). "Particle interactions in aqueous kaolinite suspensions III. Sedimentation volumes." *J. Colloid Interf. Sci.*, 60(2), 331-336.

Michaels, A. S., and Morelos, O. (1955). "Polyelectrolyte Adsorption by Kaolinite." *Ind. Eng. Chem.*, 47(9), 1801-1809.

O'Brien, N. R. (1971). "Fabric of Kaolinite and Illite Floccules." *Clay. Clay Min.*, 19, 353-359.

Palomino, A. M. (2004). "Fabric Formation and Control in Fine-Grained Materials," Ph.D. dissertation, Georgia Institute of Technology, Atlanta, Georgia.

Palomino, A. M., and Santamarina, J. C. (2005). "Fabric Map for Kaolinite: Effects of pH and Ionic Concentration on Behavior." *Clay. Clay Min.*, 53(3), 209 - 222.

Rand, B., and Melton, I. E. (1977). "Particle Interactions in Aqueous Kaolinite Suspensions I. Effect of pH and Electrolyte Upon the Mode of Particle Interaction in Homoionic Sodium Kaolinite Suspensions." *J. Colloid Interf. Sci.*, 60(2), 308-320.

Santamarina, J. C., Klein, K. A., Palomino, A., and Guimaraes, M. S. (2002). "Micro-Scale Aspects of Chemical-Mechanical Coupling: Interparticle Forces and Fabric." Chemo-Mechanical Coupling in Clays: From Nano-Scale to Engineering Applications, C. D. Maio, T. Hueckel, and B. Loret, eds., A.A. Balkema, Lisse, Maratea, Italy, 47 - 64.

Schofield, R. K., and Samson, H. R. (1954). "Flocculation of Kaolinite Due to the Attraction of Oppositely Charged Crystal Faces." *Faraday Soc. Discuss.*, 18, 135 - 145.

Siffert, B., and Fimbel, P. (1984). "Parameters Affecting the Sign and the Magnitude of the Electrokinetic Potential of Calcite." *Colloid. Surface.*, 11, 377-389.

Sposito, G. (1989). *The Chemistry of Soils*, Oxford University Press, New York.

Stumm, W., Sigg, L., and Sulzberger, B. (1992). *Chemistry of the Solid-Water Interface : Processes at the Mineral-Water and Particle-Water Interface in Natural Systems*, Wiley, New York.

van Olphen, H. (1977). *An Introduction to Clay Colloid Chemistry : For Clay Technologists, Geologists, and Soil Scientists*, Wiley, New York.

Wang, Y.-H., and Siu, W.-K. (2006). "Structure characteristics and mechanical properties of kaolinite soils. I. Surface charges and structural characterizations." *Can. Geotech. J.*, 43(6), 587-600.

Yuan, J., and Pruett, R. J. (1998). "Zeta Potential and Related Properties of Kaolin Clays from Georgia." *Miner. Metall. Proc.* (February), 50-52.