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Comparative study of mechanical activation of molybdenite (MoS₂) with and without magnesium (Mg) additionJ. Temuujin^{1*}, N. Setoudeh², N.J. Welham³¹*Institute of Chemistry and Chemical Technology, MAS, Peace avenue, Ulaanbaatar 13330, Mongolia*²*Materials Engineering Department, Yasouj University, Yasouj 75918-74831, Iran*³*West Australian School of Mines, Curtin University, Australia*

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Abstract: Molybdenite concentrate was mechanically activated in the presence of magnesium metal using a planetary mill in order to try to form elemental molybdenum. A sample milled for 90 min in planetary mill showed almost the same structural distortion as after 50 h in a tumbling mill, neither showed the presence of molybdenum metal. However, molybdenite milled together with magnesium showed more amorphization than separately milled molybdenite. Despite the apparent lack of reaction, molybdenite showed higher solubility in dilute HCl after milling with magnesium than without.

Keywords: molybdenite, mechanical activation, mechanochemical reduction, magnesium, solubility

INTRODUCTION

Molybdenum is a strategic metal used mostly in metallurgical applications and catalyst. The main mineral used for obtaining of molybdenum is molybdenite (MoS₂). Molybdenite processing includes hydrometallurgical [1] or pyrometallurgical [2, 3]. Molybdenite itself is highly resistant to acid leaching and is roasted to form soluble molybdenum oxide in order to process it commercially. The roasting stage includes the production of sulphur dioxide which has to be captured and sequestered in order to meet environmental standards. The extra unit operations required add to the capital and operating costs.

Mechanical activation has been shown to give a beneficial effect on the leaching behaviour of many minerals [4]. However, molybdenite is stable to mechanical activation due to its layered structure [5]. On the other hand, there is the possibility of a mechanochemical reaction between molybdenite and other compounds to form a new soluble compound [6]. Previous report showed that mechanical activation of MoS₂+Na₂O₂ mixtures with a planetary ball mill up to 5 h produced water-soluble sodium molybdate dihydrate (Na₂MoO₄·2H₂O). It seems that such solid state mechanochemical reaction are an interesting alternative for obtaining molybdenum compounds from molybdenite concentrate. Takacs et al., attempted to perform ball milling-induced reduction of MoS₂ with Al and despite highly favourable thermodynamics no direct reduction of molybdenite was observed [7]. But, milling induced reduction of MoS₂ may occur in other systems which have favorable thermodynamic values. The objective of the present study was to study

an influence of mechanical activation on solid-state reduction of natural molybdenite with metallic magnesium.

This report examines the effect of magnesium addition on the amorphization and morphology of mechanically activated molybdenite and its leaching behavior in a diluted acid.

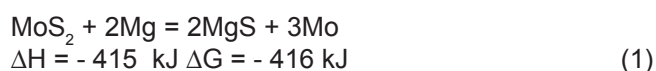
EXPERIMENTAL

Raw materials: The primary raw material used was a commercially produced molybdenite concentrate from the Sarcheshmeh deposit (Iran). The flotation concentrate was 55.55% Mo, 38.9% S, the main impurities were 1.5% Fe, 1.01% Si and 0.5% Cu. X-ray diffraction confirmed the main phase was molybdenite, with minor amounts of quartz, pyrite and chalcopyrite identified by optical microscopy. The Sarcheshmeh molybdenite concentrate is a comparatively pure raw material and is ideal for performing experiments. The magnesium used was an analytical grade chemical reagent.

A thermodynamic appreciation of the system showed the molybdenite system was predicted to react at 25°C. Thermodynamic simulation was obtained according to software HSC6 (<http://www.hsc-chemistry.net>). Figure 1 shows the predicted equilibrium compositions as a function of increasing magnesium in the system for a fixed 10 kmol MoS₂.

As is clear, there is only one reaction predicted to occur in the system, the reduction of molybdenite to form elemental molybdenum, reaction (1).

Consequently, the reactant mixtures were prepared using this stoichiometry.

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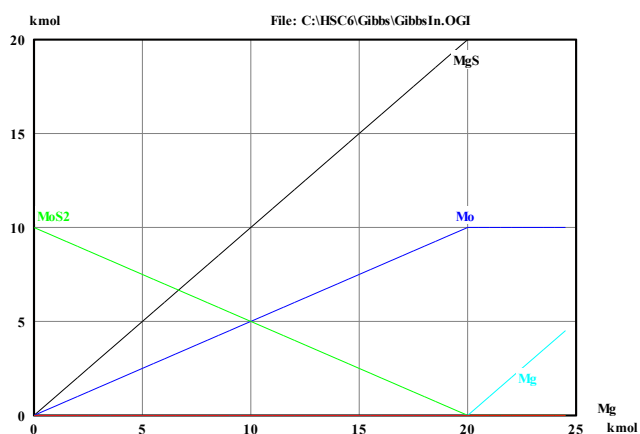


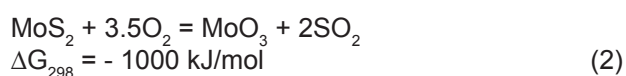
Fig. 1. Thermodynamic equilibria of molybdenite with increasing Mg at 25°C

Preliminary experiments indicated that milling in air resulted in negligible increase in molybdenite solubility in dilute hydrochloric acid. Consequently, further runs were made to examine this more closely. The initial runs were made using a tumbling mill which, even after 50 h, showed only very slight crystallite size refinement in the XRD trace. There was almost no weight loss after leaching in 1N HCl solution. Therefore, in order to increase the effect a much higher energy planetary ball mill was used with milling times of 30, 60 and 90 min. Weight ratio of balls to powder was 20:1. After milling samples were characterized by XRD (Bruker D8 Advance) and SEM (Zeiss EVO 40 XVP). The resultant powders also were leached using 1 N HCl solution, after leaching the residue was filtered, dried and characterized by XRD.

RESULTS AND DISCUSSION

Figure 2 shows the XRD traces of raw and milled molybdenite. The intensity data has been converted to \log_{10} and offset in order to better present the peaks of lesser intensity. It should be noted that even with careful sample preparation, the platy nature of molybdenite will lead to preferred orientation which results in a much higher intensity for the main peak compared to a perfectly random sample of MoS_2 . As a consequence, the relative intensities of all other peaks are significantly diminished. In this particular sample, there are only confirmed peaks for molybdenite and quartz (the small peak at $\sim 27^\circ$). The molybdenite peaks were labeled according to JCPDS card (037-1492), some of the least intense reflections have been omitted.

Thermodynamic predictions indicated that milling in air would be expected to produce molybdenum oxide by the highly favorable reaction:



However, even after 90 min there was no sign of reaction as no new peaks are evident and there was no characteristic odour of SO_2 on opening the mill.

The main effect is to weaken and broaden the peaks, an effect entirely expected due to crystallite size reduction during milling. Less obvious is the change in

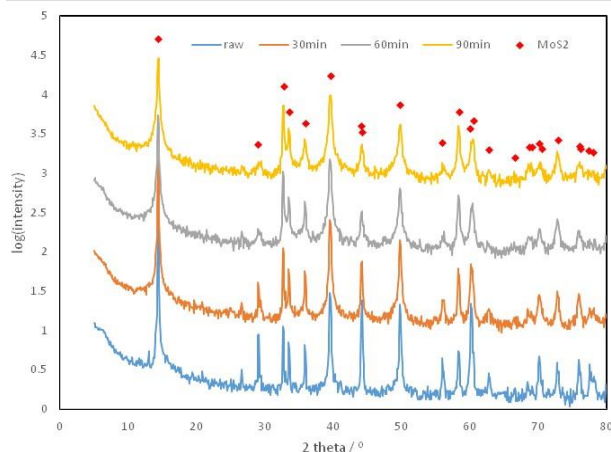


Fig. 2. XRD patterns of the raw and milled molybdenite concentrate

the ratio of the intensity of the main peak at 14.5° to the other peaks. This is relatively unusual and is related to the highly anisotropic crystal structure of molybdenite leading to preferential damage in certain crystal planes, notably the basal 002 which delaminates under stress. Figure 3 shows the XRD traces for molybdenite milled with Mg according to the stoichiometry of reaction (1). The intensity data has been converted to a \log_{10} scale in order to better show the peaks. Even after 90 min milling no new peaks can be observed implying no significant reaction had occurred, again no odour of SO_2 was noted on opening the mill. However, the intensities and widths of the molybdenite peaks indicate greater amorphization of the molybdenite in the presence of magnesium. It has been reported that during the milling of non-reactive mixtures the softer phases are amorphised more rapidly [8]. Molybdenite is considered to be one of the softest minerals (as soft as talc) and should amorphise rapidly in the presence of a harder phase. Clearly, this does not appear to be the case and is most probably related to the anisotropic crystal structure.

Longer milling also induces more amorphization of metallic magnesium as well as molybdenite. Therefore, the higher amorphization of the molybdenite in the magnesium containing mixture may be due to formation of amorphous precursor compound between molybdenite and magnesium by mechanochemical reaction as has been observed for aluminosilicates [9], though, this phenomenon is usually observed for water containing oxide systems by soft-mechanochemical reaction [10].

XRD traces of the sample milled with magnesium metal for 30 and 90 minutes before and after acid leaching are shown in Figure 4. The intensity data has been converted to a \log_{10} scale in order to better show the less intense peaks.

It is clear that the anticipated reaction did not occur to any significant extent as there are no new peaks after milling. Of the phases in reaction (1) MoS_2 and Mo are not soluble in 1N HCl so these can be expected to remain after leaching. The leached residue showed the expected absence of Mg along with a peak which has been attributed to the molybdenum oxide MoO_2 . In the residue of the 90 min milled mixture also observed

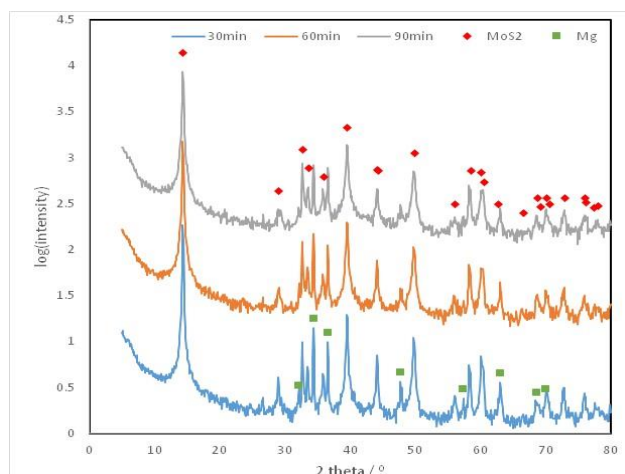


Fig. 3. XRD patterns of the milled molybdenite and magnesium mixtures

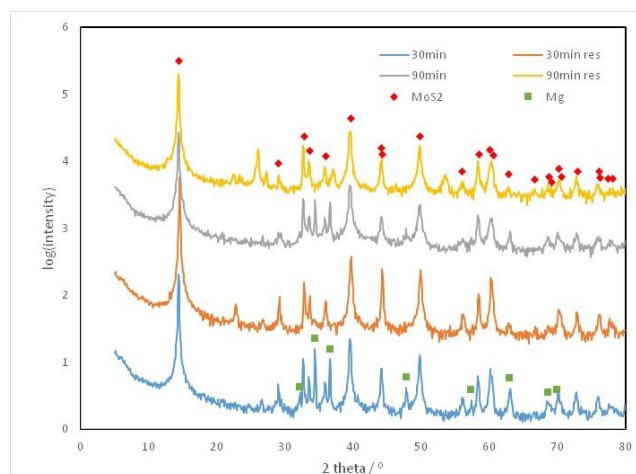


Fig. 4. XRD patterns of the milled samples and residues after leaching with 1 N HCl. Peaks not associated with MoS_2 and Mg belong to MoO_2

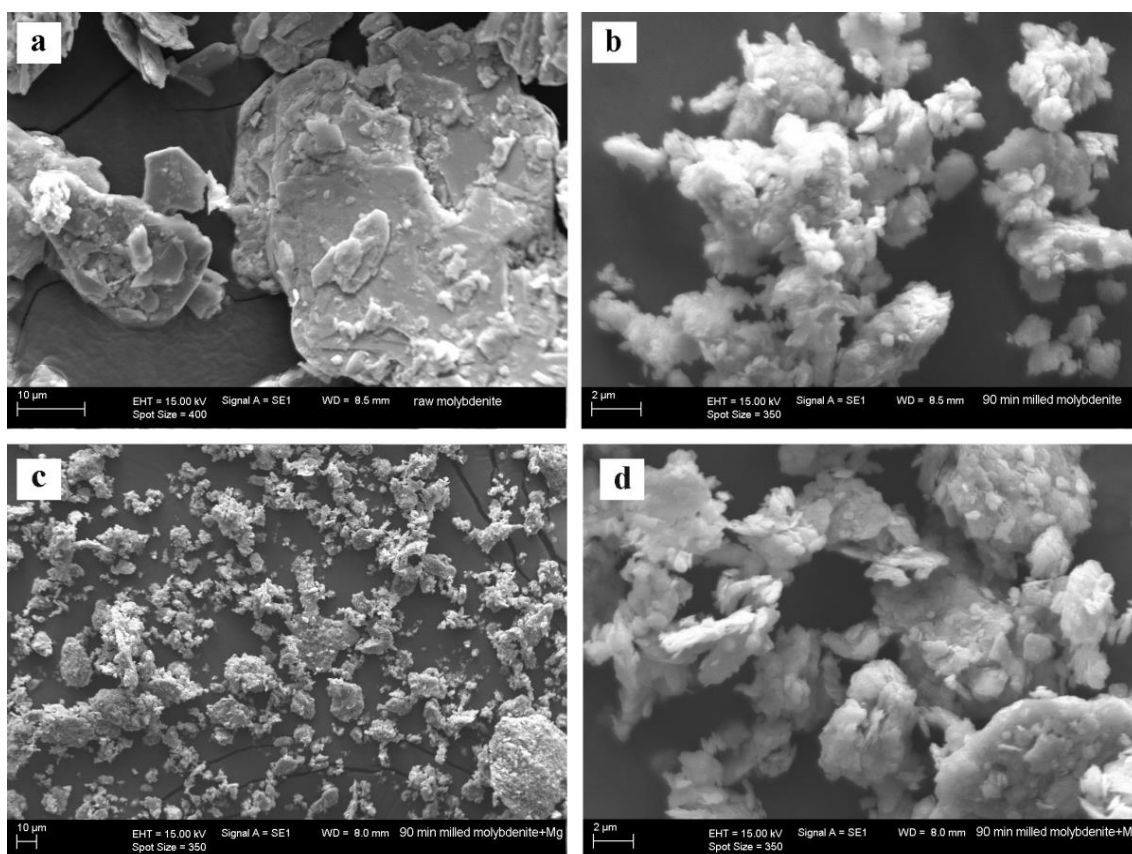


Fig. 5. SEM micrographs of the raw molybdenite (a), 90 min milled molybdenite (b), Mg added 90 min milled molybdenite with low (c) and Mg added 90 min milled molybdenite with high magnification (d).

a small peak for MoO_3 . These peaks are small and do not have any confirmatory peaks suggesting only a low abundance of these two phases.

Formation of molybdenum oxide was more evident in the 90 min residue than in the 30 min sample. Comparison with the data for the leached sample showed that the main MoS_2 peak was about the higher intensity than in unleached sample and those for the new phases are also smaller to those of the Mg in the unleached sample. Higher intensity of MoS_2 possibly due to no dilution by Mg or dissolution of the amorphous MoS_2 -Mg precursor thus leaves the fresh surface of the MoS_2 . Since the crystallite size reduction of the magnesium

containing molybdenite was not much differs from the molybdenite milled alone, that seems to be reasonable explanation.

The absence of oxide peaks from the as-milled trace would indicate that they were not present after milling but were as a result of the leaching. This implies that some of the MoS_2 was also dissolving in the acid and subsequently precipitated as MoO_2 and MoO_3 . Mass loss from the raw molybdenite in 1 N HCl was 0.4%, after milling this increased to 0.6% after 60 min and 2.6% after 90 min milling. After milling with magnesium, the mass loss after 30 min milling was 33.6%, this increased to 41% after 90 min milling. The

stoichiometry of reaction (1) indicates that only 24% of the starting mass was Mg, evidently something else in the system is dissolving. In the absence of a clear product phase the most likely candidate is the MoS_2 or some amorphous compound as it was suggested above. The present research indicates enhanced dissolution of molybdenite after milling with magnesium. Figure 5 shows SEM micrographs of the raw, 90 min air milled and Mg containing 90 min milled samples.

SEM micrographs indicated that with milling the sheet like molybdenite was converted into equiaxial particles, this confirms the preferential damage to the basal layers of the molybdenite implied in the XRD trace. Moreover, in the milled Mg-containing sample there seems to be more layered particles than air milled molybdenite. Magnesium is a ductile metal whereas molybdenite is a highly anisotropic brittle material, consequently, the Mg typically has rounded features whilst the molybdenite is more angular.

The morphology of the particles after milling was affected by the presence of ductile magnesium.

The present research also indicates that solid state mechanochemical displacement type reaction has occurred with formation of amorphous compound between MoS_2 and Mg, though, it is difficult to determine its exact chemical composition.

CONCLUSIONS

With mechanical activation in the molybdenite and magnesium metal (Mg) mixture occurs beneficial amorphization of the surface layer of molybdenite. Magnesium addition in mechanically milled molybdenite mixture doesn't cause reduction of metallic molybdenum but increase amorphization of molybdenite due to formation of amorphous compound between molybdenite and magnesium. Leaching in the 1N HCl solution leads to dissolution of the amorphous compounds and precipitation them as molybdenum oxides (MoO_2 and MoO_3).

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