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CHEMICAL CORROSION OF MOLYBDENUM AND TUNGSTEN IN LIQUID BASALT,
TUFF, AND GRANITE WITH APPLICATION TO SUBTERRANE PENETRATORS

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ABSTRACT

The chemical dissolution of molybdenum, tungsten, and some of their alloys in liquid basalt, tuff, and granite has been investigated over the temperature range 1700 to 2100 K. Static compatibility tests and a limited number of fluid-motion experiments were conducted. Wet chemical, neutron-activation, and electron-microprobe analyses were used to determine compositional changes in the rock melt and on the surfaces of the metals. This study determined that tungsten was more reactive than molybdenum over a wide range of complex silicate compositions. The enhanced solubility of tungsten is discussed in terms of some simplified thermodynamically possible reactions. The detailed mechanism of dissolution, however, cannot be totally explained although correlations with, e.g., the initial rock ferric-ferrous ratio, have been obtained.

A simplified geometric model has been developed for the determination of surface recession rates on Subterrene penetrators. Experimental data were used in applying the model. The limitations of experimental solubility data for performance predictions under field operating conditions of Subterrene penetrators are discussed.

The results of qualitative compatibility tests made with selected high temperature-high strength metals and alloys, intermetallics, and ceramics are summarized.

I. INTRODUCTION

Various rock-drilling concepts and methods, commercially operative and proposed, standard and experimental, have been reviewed and evaluated by Maurer,¹ who also mentions drilling by means of a progressive rock-melting technique. The feasibility of rock-melting drills had been explored in 1960-1962 at the Los Alamos Scientific Laboratory (LASL) where a device, called a Subterrene, was invented.² Serious engineering development however began only in 1971.

Although conceptually simple, the Subterrene system has required a multi-disciplinary approach for development beyond the stage of a laboratory curiosity, as summarized by Hanold.³ Materials development and attendant corrosion testing occupy an

important role within this program, whose major objective is the development of a materials technology that would permit one to build (long-life) penetrators and to predict their service life.

Rocks are basically complex mixtures of individual silicate minerals and their solid solutions, entrapped gases, liquids and trace-element impurities. When rocks are heated, gases are evolved progressively in increasing amounts until the rock fuses. Melting is not as sharply defined as for pure minerals or compounds, but rather occurs over a relatively large, finite range. Further, the melting range* of a rock is typically lower than the melting

*In a strict geochemical sense, melting includes the range from the first appearance of liquid to the disappearance of the last remaining crystal.

point of many of its components, thus representing a multi-component eutectic effect. Most rocks melt between 1250 and 1500 K at ambient pressures, and a few assemblages of minerals melt at even lower temperatures. It is this relatively low melting range of most rocks that makes the Subterrene concept attractive, because today's technology offers materials with significantly higher melting points.

However, sandstones and quartzites melt at considerably higher temperatures, in some cases approaching the melting point of quartz (SiO_2 , ~ 2000 K); and several rock types, such as the dolomite-limestones, normally decompose upon heating to form high-melting-point reaction products. This latter class requires unique Subterrene engineering designs.

By defining a general melting range we are able to choose suitable materials for the melting body (penetrator) of the Subterrene system. This resistively heated device is designed to achieve certain penetration rates in various rock melts. The cutaway section of an early penetrator is shown in Fig. 1. The high temperatures produced within the penetrator required exceptional materials to maintain structural and physical integrity as well as a significant

degree of chemical inertness for extended periods of time. Other factors, e.g., heat transfer, general physical and creep strength at high temperatures, fabrication capability, and surface hardness must be considered. Surface hardness is of importance because the penetrator surface is not only subjected to chemical corrosion but is also exposed to mechanical erosion. These considerations and the definition of application goals led to a design temperature range for penetrator surfaces at 1700 to 1900 K. Laboratory tests and small-scale operational runs indicated that molybdenum (Mo) and tungsten (W) are the most promising penetrator materials under the stated conditions.

The silicate mineral components of rock are geochemically characterized in terms of metal oxides, as are the components of ordinary glass. Rock melts can be chilled to the glassy state like the melts of synthetic glasses and can be treated similarly, e.g., by annealing. Therefore, metals and alloys useful to the glass industry were also considered in our investigations although Subterrenes operate under more severe conditions (e.g., higher temperatures) of greater variability. Molybdenum and tungsten have proven to be suitable for various types of glass-handling and glass-melting equipment, but tungsten has been rarely used due to higher costs. Under suitable atmospheres, both metals are reasonably corrosion resistant to many synthetic-glass compositions.

Virtually no data, however, are available about the corrosion resistance of Mo and W to natural rock melts. Pecoraro, et al.⁴ have reviewed corrosion data for Mo and W in some molten oxides, including one-component systems (e.g., B_2O_3 , Al_2O_3 , and SiO_2) and a few simple binary oxide melts. They concluded that direct elemental solubility in these particular melts was negligible and that the solution that did occur was due to oxidation mechanisms. Viscosity measurements at very high temperatures made with Mo and W crucibles to hold molten SiO_2 ^{5,6} indicated only minor solubility at temperatures between 2200 and 2600 K. The solubility of Mo has also been measured in a few CaO-SiO_2 melts^{7,8} of variable composition and in a nonferrous glass at ~ 1700 K.⁹ In most cases solubility was low.

Biggar¹⁰ has measured a Mo solubility of 0.3%

Fig. 1. Cutaway section of a Subterrene penetrator.

at 1573 K in a reducing atmosphere for an iron oxide-containing glass. The study of melts containing iron oxides or silicates has always been difficult because corrosion increases markedly as iron content becomes significant. Further, it has been shown¹¹ that the oxygen fugacity of the system strongly influences the potential reactions that may occur in both synthetic and naturally occurring iron oxide-containing melts.

Our investigation was conducted to provide information about penetrator corrosion in natural rock melts. These melts were prepared mostly from iron oxide-containing rocks such as basalt, as well as from the more siliceous rocks such as tuff and granite. Initial objectives were to determine:

- the solubility of Mo, W, some of their alloys, and other materials;
- the temperature dependence of their solubility;
- if possible, the kinetics and mechanisms of solution.

Solubility data obtained between 1700 and 2100 K were converted to areal mass loss information of pertinent interest to the engineering aspects of the Subterrene program. The relationships and limitations of the data with respect to field operation of the Subterrene are discussed.

II. EXPERIMENTAL INVESTIGATIONS

Two general techniques, static compatibility testing and dynamic testing, were utilized in our experimental program. The greatest effort was expended on static experiments. Data obtained from the dynamic experiments were limited due to termination of the investigation.

A. Static Experiments

The static experiments consisted simply of melting a rock sample in a crucible of the desired metal and holding the system at temperature for a given time. Radio-frequency induction heating was used. Following this treatment, the crucible was examined metallographically for corrosion, and samples of the quenched glass were taken for analysis.

The experiments were conducted as follows. A crucible of the desired metal or alloy was cleaned mechanically, then outgassed at 10^{-4} Pa (10^{-6} torr) for a few minutes at ~ 2000 K. Crucibles were typically ~ 25 mm high, had an o.d. of 19 mm and

walls 1.6 mm thick. A sight hole ~ 1.6 mm diam allowed reading of interior temperatures with a calibrated optical pyrometer.

After vacuum outgassing, the crucible was removed from the furnace, weighed, and loaded with 2 to 5 g of rock powder. These rock-powder samples had been crushed, sieved to a powder size of 80 to 120 mesh, and blended for uniformity. Chemical and mineralogical analyses of the various rock powder samples are shown in Tables I and II.

The crucible and contents were reweighed before positioning within the heating system (see Fig. 2). Attempts at immediate melting of the rock, however, continually resulted in ejection of the powder from the crucible and preliminary vacuum outgassing was found necessary to overcome this problem. The temperature was gradually raised to between 1000 and 1200 K over a period of some hours in a 10^{-3} Pa (10^{-5} torr) vacuum. Weight losses (in the rock sample) during this procedure amounted to 0.5 to 1%.

After the sample had cooled, an inert gas was added to increase system pressure to 50 - 70 kPa (~ 0.5 atm). Helium which had been passed over Ti turnings at 1100 K was used. Gas chromatographic analysis indicated a maximum O_2 content of ~ 80 ppm; thus the maximum P_{O_2} in the system was 5 Pa ($\sim 5 \times 10^{-5}$ atm), and typically was probably an order of magnitude less. A cover atmosphere prevented destructive foaming of the melt as the sample was brought through the melting range. Pressure depended on the rock material and ranged from 100 kPa (~ 1 atm) for Hawaiian tholeiitic basalt at 1900 K, to values $\ll 25$ kPa for Bandelier tuff.

After backfilling with He gas, the crucible and rock sample were quickly taken to temperature and held for the desired period of time. Temperatures investigated included 1700, 1900, and 2100 K; time periods varied from 2 to 400 ks (0.5 to 110 h). The precision of the time measurements was ± 0.6 ks, whereas the estimated error in the temperatures was ± 15 K after correction for prism and sight-glass losses. Despite precautions, occasional foaming plugged the temperature sight hole; in these cases the temperature was estimated from the input power, which, under similar loading conditions, was closely proportional to temperature.

TABLE I

AVERAGE CHEMICAL COMPOSITION OF ROCKS USED IN CORROSION EXPERIMENTS
Wt%

Component	Jemez Basalt	Dresser Basalt	Hawaiian Tholeiitic Basalt	EPR Suboceanic ^a Basalt	Amphibolite ^b	Granodiorite ^b	Bandelier Tuff	Granite Gneiss
SiO ₂	51.7	48.2	51.3	50.1	47.9	68.4	76.6	80.3
Al ₂ O ₃	16.6	16.13	15.26	15.58	16.8	15.7	12.3	10.1
Fe ₂ O ₃	2.46	7.65	1.77	1.56	2.66	1.33	1.52	0.40
FeO	7.78	5.41	9.09	9.29	7.36	1.80	0.09	0.14
Fe _T	7.77	9.55	8.31	8.31	7.58	2.33	1.13	0.39
MgO	6.31	6.25	6.86	7.88	8.02	0.90	0.05	0.12
CaO	8.76	8.69	10.85	11.7	8.87	2.23	0.31	0.10
Na ₂ O	3.50	2.54	2.48	3.28	3.88	3.64	4.10	2.7
K ₂ O	1.00	0.96	0.52	0.25	1.52	4.49	4.56	5.2
TiO ₂	1.44	1.45	2.24	1.51	1.26	0.45	0.09	0.11
MnO	0.17	0.18	0.17	0.15	0.14	0.06	0.06	0.02
P ₂ O ₅	0.14	0.16	0.21	0.09	0.17	0.11	0.02	0.01
CO ₂	0.09	0.05	0.18	0.06	0.03	0.06	0.18	--
H ₂ O	0.15	0.38	0.04	0.08	0.01	0.01	0.09	0.05
Fe ⁺³ /Fe ⁺²	0.284	1.271	0.175	0.151	0.325	0.664	15.175	2.57
Mo ^c	5	---	---	---	< 1	< 1	3	--
W ^c	3	---	---	---	< 10	< 10	3	--

^a Samples obtained from dredging operation on a peak of the submerged East Pacific Ridge in collaboration with Sandia Corp., Albuquerque, NM, Magma Tap program.

^b Samples were obtained from a depth of ~ 750 m in collaboration with the LASL Geothermal Energy Program.

^c Analyses in parts per million.

Upon completion of the specific heating cycle, the crucible was removed from the system and weighed to determine mass losses. Any unusual visual phenomena were noted. The inside diameter of the crucible was then measured with a traveling microscope. Finally the crucible was sectioned lengthwise with one-half mounted in Lucite and was polished to a 0.5 μ m diamond finish for metallographic examination (see Fig. 3). Chemical etching was used to enhance the grain structure. The average height of the glass melt on the inside crucible walls was measured, allowing an estimate of the area of reaction, as the sum of the area of the bottom of the crucible and the cylindrical area covered by glass.

The unmounted crucible half was sectioned further with a low-speed diamond saw, and samples of

the rock-melt glass were cut out for chemical, electron-microprobe (EMP), or neutron-activation analyses.

B. Dynamic Experiments

A relative-motion apparatus added the element of flow to the static tests. This modification consisted of a spinning rod introduced into the melt. In contrast to the static tests, a tungsten-mesh resistance furnace was used for the motion experiments. This furnace had a 64 by 152-mm hot zone, was fitted with suitable feedthroughs for rotary motion, and allowed operation in vacuum or in inert-gas atmospheres to temperatures of 2350 K. A dc motor turned the rotary feedthrough shaft, which in turn was coupled to a shaft of the crucible material. The shaft outer diameter was initially 6.35 mm and

TABLE II

MAJOR MINERALOGICAL COMPOSITION OF ROCKS

Type	General and Modal Analyses*
Dresser basalt	Plagioclase (50) pyroxene-amphibole and olivine (45), magnetite (5).
Jemez basalt	Olivine (41), plagioclase (47), magnetite (6), altered olivine and plagioclase (6), clinopyroxene (small).
Bandelier tuff	Quartz (11), sanidine (11), pumice ash, glass, montmorillonite, hornblende, and miscellaneous (remainder).
Suboceanic basalt	Plagioclase, pyroxene, olivine, magnetite.
Granodiorite	Biotite (6), microcline (30), plagioclase (27), quartz (31), altered plagioclase (3), miscellaneous (3).
Granite gneiss	Quartz (major), potash feldspar (orthoclase or microcline).
Hawaiian basalt	Plagioclase, pyroxene, magnetite, possible olivine.
Amphibolite	Biotite (22), hornblende (44), plagioclase (20), altered plagioclase (11), quartz (1), miscellaneous (2).

* Modal analyses, where available, are quantitative petrographic analyses; volume percentages are given in parentheses.

Fig. 2. Induction-heated furnace and high-vacuum system for static tests.

Fig. 3. Typical sample mounted for metallurgical and areal examinations.

fitted through a slightly larger hole in the crucible lid. The crucible and the lid were mounted on a linear-motion vacuum feedthrough and could be raised or lowered ~ 25 mm. The rotating shaft turned at speeds up to 50 rpm. The overall system is shown in Fig. 4; details of the stirring-rod assembly are shown in Fig. 5.

The experiments performed in the rotary motion apparatus differed somewhat from the static experiments. The rock in the test crucible was "premelting" in the heating system at ~ 1425 K after outgassing as previously described. The cooled crucible and sample were then transferred to the rotary motion apparatus. After suitable alignment of crucible and stirring rod, the system was evacuated, then back-filled to 60 - 70 kPa with purified helium. The sample was brought up to temperature, and the rotating stirring rod was lowered into the melt. Because of thermal expansion of the support rods and the stirring rod, the height of the crucible and melt relative to the stirring rod had to be adjusted periodically.

At termination of the run, the rotating stirring rod was removed from the crucible, if possible. The high viscosity of tuff melt, however, prevented such

Fig. 4. Overall view of tungsten resistance furnace and associated equipment.

Fig. 5. Stirring rod and crucible setup in tungsten resistance furnace.

removal. After cooling, the sample was taken from the furnace, sectioned, mounted, and analyzed as described previously.

C. Corrosion Measurements

1. General. A variety of techniques were considered for estimating the corrosion rates: X-radiography for measurement of dimensional changes, EMP analysis for material identification and determination of concentration profiles in the glass, and chemical or neutron-activation analysis for determination of metal concentration in the rock-melt glass. Because the observed corrosion was not severe (in Mo, W, or their alloys) X-radiography was not continued. Likewise, because of a lack of suitable standards, EMP analysis was used primarily for identification of the various new phases that appeared during the experiments. Limited quantitative results pertaining to concentration profiles were obtained. Analyses were done by chemical (spectrophotometry) and neutron-activation methods, both of which had been developed for the determination of Mo and W in both rocks and rock glasses. Results were cross-checked periodically. A brief description of both methods follows:

2. Spectrophotometric Method. In this method, the powdered sample (~1 g) was first dissolved in a 15/1/1 vol% mixture of HF/HNO₃/H₂SO₄; the solution was then fumed to dryness and redissolved in 6 N HCl. The Mo was complexed and extracted by using a one percent solution of toluene -3,4-dithiol in pentyl acetate. Molybdenum absorbance was measured at 685 nm. A similar solution and the same reagent was used for W extraction except that the solution was heated to ~360 K, the acidity was increased to ~10 N, and the W was reduced to the pentavalent state with titanous chloride. Tungsten absorbance was measured at 640 nm. Accuracy was estimated to be ~± 5%, and precision ~± 10%.

3. Neutron-Activation Method. The neutron-activation analysis technique, using LASL's Omega West Reactor (OWR) for irradiation and special counting and data-reduction facilities of CNC-11, allowed use of smaller samples, weighing typically 20 to 100 mg.

Briefly, the technique uses an (n, γ) reaction of a stable isotope of the desired element to produce a gamma-emitting isotope. For our experiments, the reactions were those shown in Table III.

The samples were weighed, packaged in quartz tubes and irradiated in the OWR for ~8 h at a neutron fluence of 2×10^{16} n/m²·s (1.2×10^{14} n/cm²·min). Originally, total irradiation was given in terms of MWh exposure; however, subsequent determinations of flux variations led to the positioning of a chromium flux tracer next to each sample, which allowed normalization to the flux used during calibration with known samples.

Following irradiation, the samples were removed from the holder and mounted in counting platens. An energy spectrum (number of counts in 20 minutes versus energy of gamma ray) was obtained by using a

pulse-height analyzer and a lithium-drifted germanium detector. Output was analyzed by computer to obtain the activity corrected for elapsed time since irradiation. This number is proportional to the amount of metal present, the constant of proportionality having been determined with standards. In some cases counting was delayed after irradiation, because the sample was either too hot or because we had to wait for interfering radiation (e.g., sodium Compton x-rays which interfere with the Fe analysis) to die out. In either case, corrections could be made to determine the activity at time zero, i.e., during reactor irradiation. As long as counting is done within one to two half-lives of irradiation there are no difficulties; fortunately, for the relatively short-lived ¹⁸⁷W isotope, there is little interference.

From the results of analyses on known samples or on duplicate runs, the errors of analyses have been estimated as follows:

Material	Accuracy, %	Precision, %
Molybdenum	± 15	± 15
Tungsten	± 10	± 3
Iron	± 5	± 3

III. RESULTS

A. General

Results of this work do indeed yield solubility estimates, and some recommendations for penetrator-body materials are made. However, as will be seen in the discussions that follow, the results are difficult to interpret due to interference by, e.g., viscosity effects, vaporization, and large chemical variability in the rock melts. Consequently, only limited information regarding temperature dependence of the solubility was obtained. Simplified systems will probably have to be studied before the kinetics or mechanisms of solution can be precisely defined.

The majority of our data are measurements of the amount of metal dissolved in the rock-melt glass after a given heat treatment at specified temperatures and times under static test conditions. The limited dynamic experiments tended to corroborate the static-test results. The solubility of Mo and W, of some of their alloys, and of a few other substances in various basalts, Bandelier tuff, and

TABLE III
NEUTRON ACTIVATION ANALYSIS

Reaction	Half-Life	Counted Gamma Ray Energy, (keV)
Fe ⁵⁸ (n, γ) Fe ⁵⁹	45 d	1098, 1293
Mo ⁹⁸ (n, γ) Mo ⁹⁹	66 h	140
W ¹⁸⁶ (n, γ) W ¹⁸⁷	24 h	687

some forms of granite was examined over the temperature range 1700 to 2100 K for time periods of 2 to 400 ks. General discussions of the results follow. Specific data are presented in Appendix A.

B. Molybdenum in Jemez Basalt

The solubility of Mo in Jemez basalt averaged 0.25 wt% for heating times ≤ 87 ks, but the data scatter of $\pm 30\%$ precluded assigning either a temperature or time dependence to the solubility. An upper limit for the heat of solution* may be estimated at ~ 40 kJ/mol. Thus, the solubility of Mo in Jemez basalt may be approximated as

$$S \text{ (wt\%)} \approx 3.0 \exp \left[\frac{-40,000}{RT} \right]$$

This calculation is complicated by the observation that there is a pronounced depletion of Mo in molten basalt with time, particularly at the higher temperatures. Some mechanism is operative which removes Mo from the melt. Because of its relatively larger vapor pressure at these temperatures, MoO_3 vaporization is suspected. Note, however, that Mo depletion (in glass melt) occurred even in sealed capsules. It is suggested that a transport cycle is operative, in which MoO_3 is vaporized from the melt and then reacts with the Mo of the upper crucible to form the less volatile MoO_2 according to the equation

Evidence of Mo etching in the upper parts of the crucible, the appearance of golden to dark-red deposits of MoO_2 on crucible outer lids, and

* Assuming that the solubility is given by the expression:

$$S = S_0 \exp (-E_s/RT)$$

where S = solubility, arbitrary units

E_s = heat of solution, kJ/mole

R = universal gas constant, 8.314 J/mole·K

T = absolute temperature, K

and assuming that no definite variation of Mo solubility was observed within a data scatter of $\pm 30\%$, the maximum E_s which does not contradict this observation, is given by:

$$E_s = RT^2 \left(\frac{d \ln S}{dT} \right) \approx RT^2 \left(\frac{\Delta \ln S}{\Delta T} \right) = RT^2 \left(\frac{\ln 1.35 - \ln S}{200} \right) \approx 40 \text{ kJ/mol.}$$

anomalously high Mo concentrations in bits of glass melt that had solidified in the upper regions of the crucible tend to support this view of a transport mechanism.

The scatter in the data of the static experiments is generally due to inhomogeneity of the melt (see Appendix A). Swirls of brown color were seen in the solidified rock-melt glass and were identified by EMP analysis as regions of high Mo concentration (see Fig. 6). These swirls are randomly distributed in the melt and are likely caused by convection currents. Swirls were not evident in glasses from the stirred experiments, and analyses at different levels of rock-melt glass revealed that the concentration of metal was uniform. Molybdenum concentrations were nonetheless about the same as in the static tests.

C. Molybdenum in Bandelier Tuff

Molybdenum had a solubility one order of magnitude less in tuff than in Jemez basalt; Mo concentrations of 0.03 ± 0.015 wt% were observed in the tuff glass. As with the basalts, dark streaks were noted, primarily in thin layers adjacent to the crucible surfaces. There was an interesting difference in fracture behavior between the tuff glass and the basalt glass in Mo containers. Whereas stress on a basalt glass/Mo bond almost always caused separation at the glass/metal interface, the same test on a tuff glass/Mo bond resulted in fracture of the glass a short distance (~ 1 mm) from the interface.

A few experiments on deep granodiorite and granite gneiss yielded solubilities comparable to those observed in tuff.

Fig. 6. Glass melt inhomogeneity as shown by swirl patterns in rock glass.

D. Tungsten in Jemez Basalt

Tungsten is more soluble (by weight) in basalt than Mo, by a factor of ~ 5 to 10 over the various temperature ranges. There is an increase in tungsten solubility with temperature; a treatment of the solubility data obtained at long times yielded a heat of solution for tungsten in basalt of ~ 80 kJ/mol. Again, the approximate expression of W in Jemez basalt is

$$S \text{ (wt\%)} \approx 240 \cdot \exp \left[\frac{-80,000}{RT} \right]$$

There is no definite evidence of depletion with time of the W dissolved in the melt. Convection swirls of high W content were similar to those noted in Mo experiments.

E. Tungsten in Bandelier Tuff

Tungsten solubilities in the range of 0.4 to 1.6 wt% were determined at 1900 K only. Segregation of the dissolved W in the rock-melt glass was evident, as determined by coloration and chemical analysis. Solubilities were of the same order as in basalt at 1900 K.

F. Metals in Basalt Series

An investigation of W, Mo, and alloy solubilities in a series of basalts having similar silica contents was undertaken. The chemical and mineralogical compositions of these basalts, i.e., Dresser, Jemez, Hawaiian tholeiite, and East Pacific Ridge (EPR) suboceanic, are listed in Tables I and II. These basalts have similar viscosities (estimated at ~ 1 N·s/m² at 1900 K), and differences in solubility may therefore be ascribed primarily to chemical differences of the rock.

Metal solubilities in the basalt series at 1900 K range as high as 3.5 wt% for W and 1.4 wt% for Mo, as shown in Fig. 7. The data are presented as a function of the $\text{Fe}^{+3}/\text{Fe}^{+2}$ ratio as a possible correlation. Data for Mo-30W and Mo-TZM alloys are also shown. The limited data suggest that some alloying may inhibit reaction, e.g., of Mo-TZM. The amounts of Mo and W dissolved from the Mo-30W alloy are approximately proportional to the respective weight fractions in the alloy.

IV. DISCUSSION

The experimental data for Mo and W solubility in various rock melts are presented in Table IV

Fig. 7. Solubility data for molybdenum, tungsten, and alloys in various basaltic compositions.

together with the results for less complex melts obtained by other investigators. Generally, the results for Mo in Jemez basalt and Bandelier tuff fall within the range of other measured Mo values. However, the results for W are considerably higher than the data reported for pure silica at higher temperatures, suggesting that at lower silica concentrations the solubility of tungsten is enhanced, possibly due to a viscosity effect. The data also suggest that certain glass components, e.g., PbO or FeO, may be very effective in increasing metal solubility. Solubility data to be presented later show a correlation with Fe content of the melt.

The significant observation of this work is the higher reactivity of W relative to that of Mo over a wide range of complex silicate compositions. This difference is somewhat unexpected, although in work by Amosov et al.¹⁴ on the wetting of W and Mo by melts of the systems $\text{K}_2\text{O}-\text{SiO}_2$ and $\text{K}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3$, differences in the character of the reactions of W and Mo with the melts are discussed.

The difference in solubility has two possible causes if it is assumed that solution of the metal

TABLE IV
MEASURED SOLUBILITIES OF METAL IN GLASS

Metal	Glass Composition, wt%							Time, ks	Temp, K	Metal In Glass, wt%	Ref.
	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	Other				
Mo	56	23	5.0	10.0	1.5		B ₂ O ₃ -4.5		1673	0.02	9
Mo	57	1.5			4.5	8.0	PbO-29.0		1673	0.96	9
Mo	44.4	10.8	17.8	4.3			FeO-22.8	23	1573	0.3	10
Mo	65		35					36	2073	0.04	7
Mo	40						BaO-60	11	2073	0.47	12
Mo	*		*					11	2073	0.03	12
Mo	*						TiO ₂	~10	2073	0.01	12
Mo	~60	~50						108	>1873	<0.15	13
Mo	51.7	16.6	8.8	6.3	3.5	1.0	Fe _T -7.7 [†]	<87	1900	0.24	this work
Mo	76.6	12.3	0.3		4.1	4.6	Fe _T -1.1 [†]	≤87	1900	0.04	this work
W	100							18	2273	<0.1	6
W	100							14-29	2573	0.001-0.06	5
W	51.7	16.6	8.8	6.3	3.5	1.0	Fe _T -7.7 [†]	≥87	1900	~1.5	this work
W	76.6	12.3	0.3		4.1	4.6	Fe _T -1.1 [†]	11	1900	0.4-1.6	this work

* Oxide is a component, but fraction not given.

[†]_T means total.

is affected by initial oxidation followed by dissolution of the oxide in the melt, as suggested by Pecoraro et al.⁴ Either the initial oxidation kinetics are substantially different, with W oxidation more rapid, or, if the rate of oxidation exceeds the rate of diffusion of metal ions in the melt, a very low diffusion coefficient of Mo in the melt might inhibit solution because of a saturated boundary layer adjacent to the crucible wall. The latter explanation is not considered viable because glasses obtained after 60-90 ks were reasonably homogeneous with respect to Mo distribution. Furthermore, in the stirred experiments, where some additional mixing occurred, the measured amounts of dissolved Mo were essentially equal to those obtained in the static tests. Samples taken from very thin layers adjacent to the bottom crucible surface showed no abnormally high Mo solubility. Finally, visual and EMP examination revealed the presence of swirls of high Mo concentration inside the crucible (see Fig. 6).

The free energies of formation, ΔG_f° , per mol of oxygen atoms are given in Fig. 8 for the di- and trioxides of Mo and W; data for wustite (Fe_{0.947}O) and hematite (Fe₂O₃) are included. On the basis of stability considerations, one may conclude that the driving potentials for oxidation reactions involving MoO₂ or WO₂ are not significantly different. If oxidation proceeds to the trioxides, then larger differences of free energies are evident and in the correct order (WO₃ more stable). As one possible example, consider the reaction of the crucible material with Fe₂O₃ in the melt to give the metal trioxide and FeO (liquid at experimental temperature):

The free energies of this reaction for M = Mo and W are shown in Table V. The free energies for these reactions represent reasonably large potentials for driving the reaction to the right. Thus, only if

Fig. 8. Free energies of formation, ΔG_f° , of molybdenum, tungsten, and iron oxides.

there is a very large difference in activity between the two trioxide species in solution, can these thermodynamic calculations justify the observed differences in solubility. There is no *a priori* reason why the activities should be so different. The reader is cautioned, however, that the actual system is extremely complex, and that the use of explanations involving discrete entities such as Fe_2O_3 may be misleading.

Other comparisons, based on the free energies of formation of the component oxides in these rock

TABLE V
FREE ENERGIES OF TRIOXIDE REACTION

Temp, K	ΔG_R° , kJ/mol		
	MoO ₃ (l)	WO ₃ (l)	Difference
1700	-177.9	-233.7	55.8
1900	-234.7	-284.7	50.0
2100	~-293	-339.0	~46.0

systems also suffer from similar ambiguity. Some values of free energy per mol of oxygen atoms, ΔG_f° , are listed in Table VI in order of decreasing stability. A metal will react, though at an unspecified rate, with any oxide appearing below the metal oxide. For example, one would predict that Mo or W would react with Na_2O and K_2O . Reactions of this type, e.g.,

have been proposed by Pask and his co-workers for various glass-metal systems.¹⁵ Weight-loss measurements on early experiments suggested reactions of this type; however, subsequent determinations of the post-test Na_2O and K_2O composition of the cooled glass melts showed that within experimental error, no Na or K was lost except for a few runs at 2100 K for long times (> 100 ks). Furthermore, if these reactions were part of the dissolution mechanism of Mo or W, one might expect a greater solubility in tuff melts than in Jemez basalt melts because of higher Na_2O and K_2O contents in the former. No definite evidence of such an enhancement was observed.

TABLE VI
FREE ENERGIES OF FORMATION OF GLASS COMPONENT OXIDES¹⁶

Oxide	$-\Delta G_f^\circ$, kJ/mole Oxygen Atoms		
	1700K	1900K	2100K
CaO(s)	452.8	418.9	380 (est)
BaO(s)	395.4	376.7	344 (est)
Al ₂ O ₃ (s)	377.4	356.0	334.7
MgO(s)	382.1	341.1	300.4
TiO ₂ (s)	318.2	300.5	282.1
SiO ₂ (l)	304.6	285.2	266.0
B ₂ O ₃ (l)	288.8	274.9	261.0
FeO(l)	164.1	154.1	143.2
MoO ₂ (s)	147.2	131.6	116.4
WO ₂ (s)	144.7	128.4	112.4
WO ₃ (l)	139.1	126.6	114.1
Fe ₂ O ₃ (s)	130.0	113.3	95.9
MoO ₃ (l)	121.2	109.9	98 (est)
Na ₂ O(l)	120.8	73.8	27.9
K ₂ O(s)	47.3	- 0.8	-

Post-test composition analyses uniformly showed that essentially all ($\sim 98-99\%$) ferric iron (Fe^{+3}) was reduced to ferrous iron (Fe^{+2}). Estimates of the test atmosphere oxygen partial pressure, P_{O_2} , based on the helium gas impurities or on extrapolations of measured oxygen fugacities over basaltic magmas^{17,18} yield values of $\log P_{\text{O}_2} = 4 \pm 1$. Such P_{O_2} values are reasonable for the reaction, $2 \text{Fe}_2\text{O}_3 \rightleftharpoons 4 \text{FeO} + \text{O}_2$ at $\sim 1900\text{K}$. However, dilute solutions of FeO and Fe_2O_3 would be expected to have much lower P_{O_2} values ($\sim 10^{-10}$ atm, based on measured FeO and Fe_2O_3 concentrations). Hence it is suggested that Fe_2O_3 (or at least Fe^{+3}) plays a role in the oxidation of the Mo or W. Certainly the expected magnitudes of metal dissolved on the basis of the reaction

are similar to those observed experimentally. (On the basis of the above equation, 1 wt% Fe_2O_3 would create ~ 0.3 wt% MO_3 or ~ 0.5 wt% WO_3 if the reaction went completely. The presence of ferrous iron (Fe^{+2}) will inhibit the reaction to some degree.)

Measured metal solubilities at 1900K after 11 ks have been correlated with the Fe content of a variety of real and "mixed" basaltic materials. The results are shown in Fig. 9, where wt% of W dissolved is plotted versus $\left(\frac{\text{Fe}^{+3}}{\text{Fe}^{+2} + \text{Fe}_T}\right)_{\text{initial}}$ of the material. Less extensive, but similar, data exist for Mo, Mo-30W, and Mo-TZM, and show a similar trend. The significance of the correlation variable may be interpreted as the product of a capacity term, Fe_T , and a reaction term, $\text{Fe}^{+3}/\text{Fe}^{+2}$, indicative of the propensity to reaction.

The viscosities of the materials used in Fig. 9 are similar. However, the correlation breaks down, especially for Mo, when one attempts to fit data from the more siliceous materials such as tuff or granite. This failure suggests, as has been mentioned elsewhere, that the viscosity of the melt may be an important factor.

A final point concerning Fe reduction. In a number of experiments, elemental Fe was detected both as relatively pure metallic spheres and as a 1-5 wt% alloy with the crucible material. The latter was perhaps more common (liquid Fe readily alloys

Fig. 9. Solubility of tungsten in various basaltic compositions. The rock type amphibolite, which has a viscosity similar to that of basalt, has been included (see Appendix A).

with Mo and W),¹⁹ with the alloy often "growing" from the surfaces of the crucible. The spheres tended to be associated with bubble cavities, suggesting that some gas-phase reactions are altering the thermodynamics of the melt to allow reduction of ferrous iron (Fe^{+2}) to elemental Fe.²⁰ In both cases of metal appearance it is estimated that only a small fraction of the initially oxidized Fe was reduced to metal.

In summary, the measurements of Mo and W solubility in various complex mineralogical melts show that W is more soluble (by factors of 2-50) than Mo. Values for Mo were in some cases similar to those from other investigations involving less complex silicates.

The detailed mechanism of dissolution cannot yet be specified, and the enhanced solubility of W over that of Mo similarly cannot be totally explained. The difference in solubility may be due to thermodynamic stability considerations taking into account solution effects. Reduction of iron

(Fe^{+3} to Fe^{+2}) is suggested as a contributory mechanism of Mo or W oxidation. For materials of similar viscosity, a correlation of metal solubility with Fe content was obtained. The effect of gases evolved from the melt due to inter-component reaction during a given test period upon metal corrosion has not been fully investigated. It is suggested that viscosity effects play a role in the chemical corrosion of Mo and W. Effects from parameters such as dynamic flow, variable PO_2 , and surficial wetting upon solubility and mass transport have not been investigated. Under these circumstances, the data generated in these studies should be applied with due caution when comparisons are made with tests run under field conditions.

Although quantitative corrosion experiments have not yet been made under field conditions, several 50-mm penetrators were previously examined after field operation from a qualitative and metallurgical point of view. Results have been presented in an internal report.²¹ In summary, the observations suggested both a solution mode and a gas-phase mode of corrosive attack. Examples for a Mo surface are shown in Fig. 10. Surface etching, pitting, and alloys of composition Mo-(1-5)Fe and occasionally Mo-(1-5)Fe-(Ti,Si, small amounts) were also observed.

V. PREDICTION OF PENETRATOR WEAR DUE TO CHEMICAL REACTION

By using the data one can make some preliminary estimates of the wear, due to chemical action only, of an operating penetrator. A model for the recession rate on the outer surface of a cylindrical penetrator is described in Appendix B. The resulting expression for the recession rate, $\Delta r'$, is

$$\Delta r' (\mu\text{m/s}) = 10^{-3} \frac{D_p}{2} V \cdot \{1 - [1 - 4f(1+f)K']^{1/2}\}$$

where D_p = penetrator diameter, mm
 V = penetration velocity, mm/s
 $f = \delta/D_p$
 δ = thickness of dissolved metal boundary layer in glass lining, mm
 $K' = \frac{1}{H_p} \cdot \left(\frac{\rho_g}{\rho_p}\right) \alpha_p$
 H_p = penetrator length, mm
 ρ = density of glass (ρ_g) or penetrator metal (ρ_p)
 α_p = solubility (by weight) of metal in glass.

Molybdenum

(a)

(b)

Fig. 10. Examples of corrosion observed on 50-mm penetrator after field operation.
 (a) Basalt rock glass - Mo interfacial region demonstrating solution and possible gas phase corrosion. (16X)
 (b) Spherical depression in surface suggesting gas phase corrosion. (40X)

By using geometrical constants appropriate to a 75-mm penetrator, and average 1900 K values for α_p in various materials, one obtains the estimates of surface wear for Mo and W as a function of time as shown in Fig. 11. The value of δ chosen, 1.0 mm, is representative of observations on static experiments. As field data become available to better define working values of δ , it will be relatively simple to scale Fig. 11.

Fig. 11. Chemically induced surface wear of molybdenum and tungsten as a function of drilling time.

As yet, no comparison of these estimates with actual field penetrator tests has been possible. It is emphasized again that these estimates are for chemical corrosion only. If mechanical erosion can also occur, these estimates are lower limits; however, since equilibrium during operating conditions has been assumed, the estimates are upper limits. The tradeoff between these two effects is not yet known.

VI. QUALITATIVE COMPATIBILITY TESTS ON OTHER MATERIALS

A. Test Procedures

Materials other than Mo, W, and their alloys have been investigated only qualitatively. A limited number of screening tests were run on selected metals, alloys, intermetallics, and ceramics. These tests involved heating a small disk* or crucible of

*Disks were heated in Mo or W crucibles although tests made early in the program used graphite crucibles at temperatures up to 1600 K and occasionally TaC-coated graphite crucibles. The use of graphite was later discontinued when it was realized that the more fluid silicate melts transported carbon to the test material; carbon reduction of the melt was also observed.

the material to be tested with a specific rock for 3.6-7.2 ks under an inert-gas atmosphere (~ 50 -70 kPa) at both 1700 and 1900 K. Early in the program some materials were heated at ~ 1600 K, but engineering criteria were subsequently changed. Oxygen partial pressure in the system was estimated to be $\sim 10^{-4}$ - 10^{-5} atm, similar to that in the quantitative studies. A cross-sectioned sample was examined metallurgically upon test completion. Electron-microprobe examination was used for element identification within reaction zones. In those cases where reaction layers were not evident, the surface was examined, after rock glass removal, for solution effects relative to the original sample surface.

B. Test Results

1. Graphite. Of the materials tested, only graphite exhibited a non-wetting condition, i.e., contact angle $> 90^\circ$, at temperatures up to ~ 1600 K. Hence, reactivity with a melt was minimal. Higher temperatures resulted in progressively severe reactions. Reduction of the iron silicates, particularly in basaltic melts, resulted in the formation of free Fe and Fe-Si alloys. A sample of a vitreous carbon was also severely attacked in basaltic media.

2. Noble Metals and Alloys. The metals Pt, Rh, Ir, and some of their alloys were attacked generally in basaltic melts, where reducing conditions prevailed, and, where free SiO_2 was available, low-melting eutectics such as $\text{Pt-Pt}_3\text{Si}$ were formed. These tested materials would probably be more useful under fully oxidizing conditions.

3. Intermetallics. The compounds Nb_3Ir , ZrPt_3 , and HfPt_3 were tested in basalt and tuff melts. All corroded severely. Although both ZrPt_3 and HfPt_3 are very stable in a thermodynamic sense, they nevertheless reacted strongly under these test conditions. It is again probable that they would be useful under more oxidizing conditions.

4. High Melting Metals. Such metals as Ti, Zr, V, Cr, Re, and Ta were tested. Severe solution attack was exhibited by Ti, Zr, and Cr. Moderate solution attack was observed for V at 1700 K, which became very severe at 1900 K. Tantalum developed a reaction layer containing Fe and Si and possibly oxygen. Rhenium exhibited the best corrosion resistance although surface etching and discoloration were visible.

5. High Temperature-High Strength Alloys.

These alloys are of considerable interest for sustained penetrator operation.

Alloys of the type Ta-10W*, Mo-50Re, Mo-20Cr, and W-25Re in addition to such solution and dispersion-hardened alloys as W-1Hf, W-1Zr, Mo-1Hf, W-2ThO₂, W-2.5C-0.5Hf, W-4Re-2C-0.5Hf, and W-24Re-1ThO₂ were checked. With the exception of the Ta-10W and Mo-20Cr alloys, all others, within the sensitivity and interpretative limits of this type of screening test, exhibited corrosion effects equivalent to or less than the unalloyed Mo and W. In particular, alloys containing Re appeared to be more corrosion-resistant. No reaction layers were seen. Obviously, quantitative tests will be required for a better differentiation of these results. The Mo-20Cr and Ta-10W alloys acted similarly to Cr and Ta, respectively.

6. Ceramics. Selected ceramic compounds in various categories were tested with the following results.

a. Borides. Coatings of both Mo and W borides over base Mo and W were prepared by means of a commercial metallizing process. Although the precise phase and composition were unknown, these coatings were, under test conditions, severely corroded, especially in basalt.

The stable boride, ZrB₂, was investigated more thoroughly. An additional sample was heated in basalt at 1700 K for 87 ks (~ 24 h) and formed a reaction layer of ZrO₂ with Ca, Al, and Ti inclusions.

b. Nitrides. Nitrides such as B₄N, Si₃N₄, AlN, and HfN were tested. Testing of B₄N was restricted to a tuff melt at ~ 1600 K. No reaction was evident. The graphitic hexagonal crystal structure and other properties do not make this material a likely choice for penetrators. Although relatively unreactive in a tuff melt, considerable gas evolution in the presence of basalt was observed in the Si₃N₄ test. Further, Si₃N₄ intrinsically has an appreciable equilibrium vapor pressure at 1700 K. Similar results with basalt up to ~ 1650 K have been reported previously.²² Several reaction layers were observed around HfN; HfO₂ was identified as a major phase. Dissolution of the crucible wall was observed in the case of AlN.

c. Oxides. The only oxides tested included

zirconia, ZrO₂, and a low- and high-density version of alumina: Al₂O₃, with a density of ~ 97%, and (translucent) Lucalox, with a density of > 99.9%. Basalt penetrated and dissolved a low-density alumina crucible wall. Lucalox dissolved similarly, but at a much slower rate. No test was made with tuff melts. The basalt melt also penetrated the zirconia, with interesting results. Cubic ZrO₂ stabilized with CaO was reconverted to the tetragonal and monoclinic forms; but cubic ZrO₂ stabilized with Y₂O₃ retained the cubic form after heat treatment.

d. Carbides. Carbides tested included Mo₂C, SiC, WC-(12% Co-bonded), HfC, and TaC. All carbides tested were attacked to various degrees, with both solution effects noted (Mo₂C and TaC) and reaction layers formed (HfC and WC). At ~ 1600 K and possibly 1700 K, minimal reaction was observed between SiC and basaltic and tuff melts. Above these temperatures, deterioration became evident. Layers identified on HfC included HfO₂ and a mixed oxycarbide with Fe and Ti inclusions. The reaction layer observed on the WC-(12% Co-bonded) sample was predominantly recrystallized, in columnar orientation, WC with a higher-than-average Co content (Co diffusion outward) as well as containing Al, Si, Fe, and oxygen (element diffusion inward from the melt).

e. Silicides. Silicides tested included Zr₂Si, ZrSi₂, V₃Si, MoSi₂, and WSi₂. Both ZrSi₂ and V₃Si were attacked severely at 1900 K. Probably the test temperature was too close to the melting points of these materials (~ 1950 and ~ 2000 K, respectively) so that any low-melting eutectics formed would overlap or reach the critical temperature zone. Some unidentified reaction products and, perhaps, recrystallization were observed on the Zr₂Si sample. Tests at 1700 K showed that MoSi₂ held up well in basalt. Deterioration occurred with long exposures and at higher temperatures, and has been observed and reported elsewhere.²² In an unusual reversal, tuff demonstrated a more corrosive effect than basalt for this material. The silicide of tungsten, WSi₂, was attacked more severely than MoSi₂ in equivalent heating tests.

C. Summary

Virtually all materials tested exhibited some degree of corrosion when in contact with molten basalt or tuff. In general, corrosion effects in

*Alloys are in weight percent.

*Numbers denote wt%.

molten tuff, the more siliceous and lower Fe-containing rock melt, are less severe than in basalt, possibly because of the higher viscosity of molten tuff. The formation of reaction layers on the contact surfaces of the screened materials does not imply that the materials cannot be used for penetrator construction. Indeed, such layers may be desirable. A determination of whether the reaction kinetics are linear or parabolic is required. High density is also a desirable feature as a means of slowing rates.

Materials worthy of further detailed study include Mo and W alloys containing reasonable amounts of Re for general application; high-melting-point noble alloys containing Rh and Ir for possible use in more oxidizing environments, as well as intermetallics; and the ceramics; ZrB_2 , HfC, SiC, and $MoSi_2$ in the dense state for use below 1700 K and possibly higher temperature, pending corrosion rate investigations - these ceramics could also be used as coatings over base structural alloys.

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APPENDIX A
EXPERIMENTAL SOLUBILITY DATA

Experimental solubility data for various rock systems as a function of temperature and time are presented. Included are the measured metal concentration in the quenched glass melt, in wt%, and the overall weight loss in percent of the rock sample. Where meaningful, a Q/A value, i.e., total metal dissolved in the glass divided by the estimated area of reaction, in gm/m^2 has been included.

Multiple entries for a given experiment indicate analyses of samples taken from different sections of the quenched glass melt.

TABLE A-1

MOLYBDENUM - JEMEZ BASALT

1. Nominal Temperature, 1700 K

Run	Temp., K	Time, ks	Rock Glass Analysis Mo Content, wt%	Q/A, $\text{g}\cdot\text{m}^{-2}$	Rock weight loss, %
MoB-12	1706	4.0	0.25	13.6	1.0
MoB-16	1707	4.0	0.32	8.2	sealed crucible
MoB-39	1769	7.2	0.18	--	stirred expt
			0.19	--	
			0.19	--	
			0.20	--	
			0.22	--	
MoB-25	1712	11.0	0.33	18.7	0.8
MoB-10	1682	54.2	0.31	17.1	1.4
			0.44	24.4	
MoB-13	1702	87.0	0.24	13.2	2.0
			0.26	14.4	
			0.30	16.7	
MoB-27	1714	320.0	0.11	7.0	0.7
			0.12	7.4	

2. Nominal Temperature, 1900 K

Run	Temp., K	Time, ks	Rock Glass Analysis Mo Content wt%	Q/A, $\text{g}\cdot\text{m}^{-2}$	Rock weight loss, %
MoB-17	1912	4.0	0.34	9.1	sealed crucible
MoB-2	1927	4.3	0.26	8.9	6.0
MoB-41	1924	8.0	0.26	-	stirred expt
			0.27	-	
			0.27	-	
			0.27	-	
			0.28	-	
MoB-24	1914	11.0	0.25	~ 14.6	
			0.31	~ 17.8	
MoB-30	1909	11.0	0.18	10.5	sealed crucible
			0.17	9.8	
MoB-3	1877	20.0	0.23	10.4	7.0
MoB-46	1909	59.5	0.25	--	stirred expt
			0.25	--	
			0.26	--	
			0.26	--	
MoB-38	1911	60.0	0.14	9.4	1.3
			0.17	11.5	
			0.17	11.5	
			0.20	13.5	
			0.22	14.8	
MoB-4	1909	87.0	0.06	1.9	6.0
			0.31	10.8	
			0.43	15.0	
MoB-18	1912	250.0	0.047	1.3	sealed crucible
			0.025	0.7	
MoB-5	1906	400.0	0.062	2.6	12.0
			0.048	2.0	

3. Nominal Temperature, 2100 K

Run	Temp., K	Time, ks	Rock Glass Analysis Mo Content wt%	Q/A, g·m ⁻²	Rock weight loss, %
MoB-15	2120	2.0	0.41	~ 5.4	1.1
MoB-28	~2120	2.0	0.24	14.5	sealed crucible
			0.22	13.3	
MoB-11	2113	4.0	0.32	18.6	2.0
			0.41	23.8	
MoB-26	2121	11.0	0.28	16.0	1.2
MoB-29	~2120	11.0	0.20	12.0	sealed crucible
			0.21	12.8	
MoB-8	2115	21.6	0.20	8.1	18
MoB-6	2120	86.4	0.0/	3.1	21
			0.17	7.2	
MoB-9	2118	87.0	0.09	4.4	20
			0.16	1.7	
MoB-7	2123	241.0	0.027	1.2	20
			0.037	1.6	

2. Nominal Temperature, 1900 K

Run	Temp., K	Time, ks	Rock Glass Analysis W Content wt%	Q/A, g·m ⁻²	Rock weight loss, %
WB-6	1914	2.0	0.16	9.1	1.7
			0.90	51.0	
WB-3	1914	4.0	0.67	38.3	0.8
			1.07	61.2	
WB-12	1917	4.0	1.08	61.0	1.8
			1.10	62.2	
WB-24	1914	~ 4.0	1.03	--	--
			1.04	--	--
WB-5	1909	7.2	0.49	27.5	3.0
			1.08	60.7	
WB-13	1914	11.0	1.09	63.6	1.4
			1.82	106.2	
WB-14	1925	87.0	1.26	76.5	1.0
			1.41	85.6	
WB-11	1914	87.0	1.26	36.1	sealed crucible
WB-4	~1914	116.7	1.86	106.8	8.9
			2.02	116.0	

TABLE A-II
TUNGSTEN - JEMEZ BASALT1. Nominal Temperature, 1700 K

Run	Temp., K	Time, ks	Rock Glass Analysis W Content wt%	Q/A, g·m ⁻²	Rock weight loss, %
WB-1	1709	2.0	0.12	7.2	0.8
			1.54	92.9	
WB-1	1711	4.0	1.04	56.2	0.8
WB-2	1708	11.0	0.52	29.8	1.7
			1.80	103.0	
			1.47	84.1	
WB-16	1709	87.0	0.88	48.1	1.0

3. Nominal Temperature, 2100 K

Run	Temp., K	Time, ks	Rock Glass Analysis W Content wt%	Q/A, g·m ⁻²	Rock weight loss, %
WB-8	2120	2.0	0.99	56.5	0.6
			1.24	70.8	
WB-18	2121	4.0	1.31	79.1	0.8
			1.32	79.7	
			1.35	81.5	
			1.36	82.1	
WB-17	2108	11.0	1.25	70.4	1.6
			1.47	82.8	
WB-15	2122	87.0	2.56	144.2	2.4
			2.66	149.8	2.4

TABLE A-III
MOLYBDENUM - BANDELIER TUFF

1. Nominal Temperature, 1700 K

Run	Temp., K	Time, ks	Rock Glass Analysis Mo Content wt%	Rock weight loss, %
MoT-6	<1709	0.6	0.018 0.032	1.8
MoT-13	1709	4.0	0.048	1.0
MoT-9	1710	11.0	0.012 0.019	1.0
MoT-3	1703	87.0	0.013	1.0
MoT-5	1710	320.0	0.011 0.016	1.4

2. Nominal Temperature, 1900 K

Run	Temp., K	Time, ks	Rock Glass Analysis Mo Content wt%	Rock weight loss, %
MoT-7	1917	4.0	0.032	0.2
MoT-10	1915	11.0	0.039 0.086	1.0
MoT-14	1914	11.0	0.072	sealed crucible
MoT-15	1900	11.0	0.041 0.041 0.034	stirred expt
MoT-1	1905	87.0	0.021 0.023 0.024	2.0
MoT-4	1901	231.0	0.046	--

3. Nominal Temperature, 2100 K

Run	Temp., K	Time, ks	Rock Glass Analysis Mo Content wt%	Rock weight loss, %
MoT-8	2118	4.0	0.016 0.018	1.1
MoT-11	2120	11.0	0.027 0.038	1.1
MoT-2	2085	87.0	0.012 0.018 0.036	11.0
MoT-12	2118	320.0	0.010 0.010	7.0

TABLE A-IV
TUNGSTEN - BANDELIER TUFF

1. Nominal Temperature, 1900 K

Run	Temp., K	Time, ks	Rock Glass Analysis W Content wt%	Rock weight loss, %
WT-1	1907	4.0	0.52 1.61	~ 2
WT-3	1914	11.0	0.40 1.61	0.6
WT-4	1914	11.0	0.86	sealed crucible
WT-2	1914	87.0	0.41 0.75 1.51	0.5

TABLE A-V
METAL/BASALT SERIES

1. Nominal Temperature, 1910 K, Time at Temperature, 11 ks

Metal or Alloy	Solubility of Metal - wt%				
	Dresser Basalt	Jemez Basalt	Hawaiian Tholeiitic Basalt	EPR Sub- Oceanic Basalt	Amphibolite*
Mo	1.45 to 1.47	0.25 to 0.31	0.09 to 0.10	0.18 to 0.21	1.14
		0.17 to 0.18	0.10 to 0.13		0.77 to 0.85
			0.23 0.12		0.87
Average	1.46	0.23	0.13	0.19	0.91
Mo-TZM	0.88	0.11			
W	3.41 to 3.64	1.09 to 1.82	0.45	0.81	2.57 to 3.41
Average	3.52	1.46			3.0
Mo-30W:					
Mo	0.90	0.25	0.04	0.05	
W	1.31	0.38	0.08	0.16	

* Metamorphic rock composed mainly of plagioclase and hornblende encountered during LASL GTE program. Sample tested as an example of a potential deep drilling corrosion source.

TABLE A-VI
MOLYBDENUM/TUNGSTEN IN GRANITOIDAL ROCKS

Run	Crucible Metal	Rock Type	Temperature, K	Time, ks	wt% metal in glass
MoG-3	Mo	granite gneiss	1718	87	0.012 0.015
MoG-1	Mo	granite gneiss	1915	87	0.012 0.013
MoG-2	Mo	granite gneiss	2100	87	0.015 0.013
MoG-4	Mo	deep granodiorite	1900	60	0.090 0.040
WG-1	W	deep granodiorite	1914	11	1.45

APPENDIX B

MODIFIED GEOMETRIC MODEL FOR THE PREDICTION OF PENETRATOR RECESSION RATES

The original NSF-RANN proposal for the Subterranean concept presented a simplified model for estimating the rate of surface erosion on a penetrator.* This model equated the mass of metal removed from the surface of the penetrator to that found in the glass liner to obtain a value for surface recession per unit length of glass liner.

A small modification of this model has been made. Using measured solubilities of Mo and W in rock melts, we have applied the model to obtain some estimates of consolidator penetrator surface recession due to chemical effects alone.

Figure B-1 depicts a geometrical model for the glass liner formed by a consolidating penetrator of diameter D_p ; the glass layer containing the majority of the dissolved metal has thickness δ ; the total length of the liner is L . Let V_g be the volume of the glass "rind" which effectively contains all the dissolved penetrator metal,

$$V_g = \frac{\pi}{4} \left[(D_p + 2\delta)^2 - D_p^2 \right] \cdot L = \pi \delta L (D_p + \delta).$$

If ρ_g (Mg/m^3) is the average density of the metal-rich layer (or for that matter, of all the glass liner), the mass of saturated glass is given by

$$M_g = \pi \delta L (D_p + \delta) \rho_g$$

Fig. B-1. Geometrical model for a glass liner formed by a consolidation penetrator.

The total amount of dissolved penetrator wall material is then given by

$$M_p = \pi \delta L (D_p + \delta) \rho_g \cdot \alpha_p \quad (1)$$

where α_p is the concentration of metal in the glass "rind."

This metal must come from the surface of the penetrator; if we assume a right circular penetrator, the metal removed is given by

* Subterranean Project Proposal, "Development of a Tunneling and Excavation Technology Based on Rock Melting", Los Alamos Scientific Laboratory Proposal P-160 (November 1972).

$$M_p = \frac{\pi}{4} \left[D_p^2 - (D_p - 2\Delta r)^2 \right] H_p \cdot \rho_p$$

where

Δr = metal recession

H_p = penetrator length

ρ_p = density of penetrator metal

$$M_p = \frac{\pi}{4} \left[(4D_p \Delta r - 4\Delta r^2) \right] H_p \cdot \rho_p$$

$$= \pi \Delta r \left[(D_p - \Delta r) \right] \cdot H_p \cdot \rho_p \quad (2)$$

Equating Expressions (1) and (2) for M_p , and solving for Δr yields

$$\Delta r = \frac{D_p}{2} \left[1 - \sqrt{1 - 4f(1+f)K'} \right] \quad (3)$$

with $f = \delta/D_p$

$$K' = \left(\frac{L}{H_p} \right) \cdot \left(\frac{\rho_g}{\rho_p} \right) \alpha_p = \left(\frac{L}{H_p} \right) \cdot \psi$$

where

$$\psi = \frac{\rho_g}{\rho_p} \cdot \alpha_p$$

As an example, consider a consolidating penetrator with

$$D_p = 75 \text{ mm}$$

$$H_p = 180 \text{ mm}$$

and assume

$$L = 1 \text{ m}$$

$$\rho_g = 2.8 \text{ Mg/m}^3 \text{ for basalt}$$

$$= 2.4 \text{ for tuff and granite}$$

$$\rho_p = 10.2 \text{ Mg/m}^3 \text{ for Mo}$$

$$= 19.3 \text{ Mg/m}^3 \text{ for W.}$$

Using average values for α_p as determined by experiment, values of ψ for this assumed system can be calculated and are presented in Table B-1.

TABLE B-1

CALCULATED ψ VALUES IN VARIOUS ROCK MELTS AT 1900 K

Metal	$10^3 \psi$		
	Jemez Basalt	Bandelier Tuff	Granitic Rock
Mo	0.65	0.09	0.02
W	2.20	1.99	1.74

For the static experiments, observed "rind" thicknesses vary over the range 0.1 to 8.0 mm; a few field penetrators exhibited "rind" thickness of 25 to 500 μm . Using this information recession rates for the model above can be calculated. The results are presented in Tables B-II and B-III for both Mo and W.

TABLE B-II

MOLYBDENUM SURFACE RECESSION, Δr , mm/m LINER

Rock Type	$\delta = 0.1 \text{ mm}$	$\delta = 1.0 \text{ mm}$	$\delta = 10 \text{ mm}$
Basalt ($\alpha_p = 0.0024$)	3.6×10^{-4}	3.6×10^{-3}	4.1×10^{-2}
Tuff ($\alpha_p = 0.0004$)	5.0×10^{-5}	5.1×10^{-4}	5.7×10^{-3}
Granitic Rock ($\alpha_p = 0.0001$)	1.3×10^{-5}	1.4×10^{-4}	1.5×10^{-3}

TABLE B-III

TUNGSTEN SURFACE RECESSION, Δr , mm/m LINER

Rock Type	$\delta = 0.1 \text{ mm}$	$\delta = 1.0 \text{ mm}$	$\delta = 10 \text{ mm}$
Basalt ($\alpha_p = 0.0151$)	1.2×10^{-3}	1.2×10^{-2}	1.4×10^{-1}
Tuff ($\alpha_p = 0.016$)	1.1×10^{-3}	1.1×10^{-2}	1.3×10^{-1}
Granitic Rock ($\alpha_p = 0.014$)	9.7×10^{-4}	9.8×10^{-3}	1.1×10^{-1}

These recession rates are for unit distance (m) of penetrator travel; to obtain recession as a function of time, Expression (3) must be multiplied by the advance rate V (mm/s):

$$\Delta r' = \frac{D_p}{2} \cdot 10^{-3} V \left\{ 1 - \left[1 - 4f(1+f)K' \right]^{1/2} \right\} \frac{\mu\text{m}}{\text{s}} \quad (4)$$

By expansion of the square-root term,

$$\left[1 - 4f(1+f)K' \right]^{1/2} \approx 1 - 2f(1+f)K'$$

and substitution into Equation (4) one finds

$$\Delta r' (\mu\text{m/s}) \approx 10^{-3} D_p (V \cdot f) (1+f)K'$$

$$\approx 10^{-3} (V \cdot \delta) (1+f)K'$$

Thus, as long as the product $(V \cdot \delta)$ is constant, the erosion rate will be nearly constant. Further, since in general $f \ll 1$, there is little dependence on D_p . The only strong dependence on penetrator dimensions is in K' , which is inversely proportional to penetrator length.