EXISTING DATA ON SPECIFIC HEAT AND THERMAL DIFFUSIVITY OF ROCKS AND MINERALS

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Thermal diffusivity is the controlling physical parameter in the transient flow of heat by conduction. In a cartesian system of coordinates, conductive heat flow is described by the equation:

$$\rho C \frac{\partial v}{\partial t} = \frac{\partial}{\partial x}\left(K \frac{\partial v}{\partial x}\right) + \frac{\partial}{\partial y}\left(K \frac{\partial v}{\partial y}\right) + \frac{\partial}{\partial z}\left(K \frac{\partial v}{\partial z}\right) + A \qquad (1)$$

where v is temperature, t is time, ρ is density, C is specific heat, K is thermal conductivity, and A is the rate of generation of heat. When conductivity and heat generation are functions of position only, solutions exist for many spatial configurations, starting conditions and boundary conditions. The best collection of solutions is to be found in Carslaw and Jaeger (1959). Where thermal properties depend on temperature, this equation becomes non-linear, and analytical solution becomes much more difficult. Since, in practice, variation of properties with temperature is relatively minor, analytical solutions are not common, and, given modern computing facilities, numerical methods are usually adequate. If conductivity is independent of position, Eqn. 1 can be simplified to:

$$\frac{\partial v}{\partial t} = s \nabla^2 v + \frac{A}{\rho C} \qquad (2)$$

where s is the thermal diffusivity. This parameter was named by Lord Kelvin, and the equation of thermal diffusion is similar to the equation of liquid diffusion. Clark Maxwell called it 'thermometric conductivity', but this term is easily confused with 'thermal conductivity' and it has been dropped.

Diffusivity is related to other thermal properties by:

$$s = \frac{K}{\rho C} \qquad (3)$$

It is only of importance in the transient state, i.e. when temperature is varying with time. In the steady state, Eqn 2 is simplified to:

$$K \nabla^2 v + A = 0 \qquad (4)$$

and the conductivity and heat generation alone remain.

Applications to Nuclear Waste Disposal

Heat transfer within the stable upper crust of the earth takes place by two mechanisms: conduction by the solid rock and advection by water flow. Convection, the drive of water by contrasts in water density is found in hydrothermal systems of recent volcanic zones, in active spreading centres, and in sedimentary rocks of high permeability, but it is not normally found in areas of interest to the nuclear waste disposal programme.

Current research is aimed at assessing the potential for water movement around a disposal facility, with a view to reducing it to a minimum, and thus ensuring that conduction alone within the rock will control both the escape of heat from the facility and the build up of temperature within the storage area. Since the facility will impose a new heat source in an otherwise steady-state temperature field, the key thermal property is diffusivity.

The strong heat source provided by the waste will inevitably generate water movement in fractures, by both convective and vapour-pressure drive. The result of this water movement will be temperature anomalies localised around natural rock fractures. Provided that the thermal diffusivity of the rock is adequately known, the conductive temperature anomaly can be calculated, and the detection of the superimposed water-induced temperature anomalies will provide a valuable tool in the detection of water movement around a storage facility.

Determination of Diffusivity

The thermal diffusivity of rock is not uniform. Within any rock unit there may be both random and systematic variations, depending on the degree of chemical differentiation, crystal or particle size, orientation and nature of crystal boundaries, disorder in crystal lattices, cooling history if the rock is igneous and metamorphic history in shield rocks. Variations within a unit of nominally the same petrological type may be as great as 20%. A large number of measurements within any rock unit is essential, rather than a few highly-accurate determinations, in order to provide a reasonable degree of confidence in the mean.

The nominal type of rock, e.g. granodiorite, gives an ambiguous prediction from measured values at another location. It gives an indication, within about 25%, but the mean diffusivity of any type of rock varies from place to place.

There are two basic ways of obtaining data of diffusivity. One is by measurements of the individual components of Eqn. 3 and by subsequent calculation. The other is by direct measurement. Historically, the science of geothermics has had a much greater need of conductivity data than of diffusivity data, and there are a large number of conductivity values, both published and unpublished. Density of rock by petrological type is well known and uniform within about 10%. The relatively unknown factor is specific heat. A few data are available, but not enough to satisfy the statistical needs mentioned above, and not enough to provide a valid prediction of the specific heat of any rock type of interest to the waste disposal programme.

The same comments may be made about the small number of direct diffusivity data. There is no adequate substitute for direct measurement of the diffusivity of the rocks directly affecting the disposal facility.

Data of Specific Heat

Kelley (1960) derives specific heat as a temperature differential of the enthalpy, according to the formulae:

$$H_v = av + \frac{1}{2}bv^2 + cv^{-1} + d \tag{5}$$

$$C = a + bv - cv^{-2} \tag{6}$$

Where H_v is enthalpy at temperature v, C is specific heat at constant pressure, and a, b, c and d are coefficients to be determined by the optimum fit to the measured enthalpy data. Goranson (1942) presents his data in the same way. Kieffer (1980) gives calculated values of specific heat, derived by means of a model of lattice vibrations of the crystalline minerals and considerations of the deviations of the behaviour of complex crystals from the model of Debye. Since this model gives specific heat at constant volume, a correction factor is added to convert to specific heat at constant pressure. These values agree well with experimental data and both are shown in Table 1.

Table 1 summarises the values of specific heat of mineral crystals found in the literature, standardised to a temperature of 298.15°K (25°C). Units have been standardised in SI, converted from a variety of different units. The results show good agreement for most minerals. The greatest standard error of the available data for any one mineral is 2.3% for orthoclase. The variation between minerals is much greater; the lowest specific heat is 707 J/kgK for orthoclase, and the greatest is 862 J/kgK for halite.

In the pyroxene group, those minerals containing only magnesium as a cation have very similar specific heats, while wollastonite, having only calcium, has a value about 10% lower. Diopside, intermediate in chemical composition has an intermediate specific heat. The three main feldspar minerals have specific heats that vary over a range of about 10%. The two alkali feldspars have the extreme values, while anorthite has an intermediate value. The value for quartz is within the range of values for feldspars, so that the main constituents of granitic rocks have specific heats between 707 and 776 J/kgK.

The values of specific heat listed in Table 1 have been obtained by measurements on single-crystal samples, of high purity and generally free from lattice disorders. Small crystals found in igneous and metamorphic rocks, which have formed in the presence of different chemicals, and have grown to fit the space available may have physical properties that are significantly different from those of pure specimens. Some minerals, such as plagioclase, are a chemical mixture, and the physical properties may not be easily predicted from the properties of their individual members.

Derivation of rock properties from mineral properties

Since they are scalar quantities, the calculation of specific heat and density of an assemblage of pure crystalline minerals from data of the constituent minerals is a simple matter. The calculation is expressed by:

$$C = \sum_{m=1}^{M} \theta_m C_m \tag{7}$$

where C_m is the specific heat and θ_m is the fractional content by mass of the mineral m. A similar equation can be written for density, but the fractional content depends on volume rather than mass. This different base of fractional content can be avoided by combining density and specific heat to give the volumetric heat capacity that is specified by the bottom line of Eqn. 3:

$$\rho C = \sum_{m=1}^{M} \phi_m \rho_m C_m \tag{8}$$

where ϕ_m is the fractional content by volume.

In a real rock, not only are the crystals of lower purity and crystalline quality, but there are intercrystalline boundary zones of which the properties are little known. The accuracy of these predictions of density can be tested, and this will be included in a later report, but there is no data to provide a test of the accuracy of predictions of specific heat. In the authors' opinion, a reliability of about ±20% should be assumed.

Conductivity of anisotropic minerals is a tensor quantity, and the apparent conductivity of a rock made up of different minerals under random conditions of crystal size, arrangement and orientation has been summarized by Drury (1980). No such analysis is known for diffusivity, but one may assume that the conductivity models are equally valid for diffusivity. It seems probable that the diffusivity of each mineral should be calculated, followed by a model calculation to generate a diffusivity for a rock. The alternative is to make the model calculation on the conductivity and to derive by a heat capacity given by Eqn. 8, but, although the difference in results is probably small, the direct model diffusivity calculation is theoretically preferable.

The best model for conductivity of a rock is the 'geometric' model, but it is not universally adequate. All models, as described by Drury (1980), give good results in some circumstances and poor results in others. The geometric model probably is successful on more occasions than others. Like conductivity, the geometric model gives a diffusivity of rock by:

$$s = \prod_{m=1}^{M} s_m^{\phi_m} \qquad (9)$$

Results

Table 2 shows values of diffusivity, both as obtained from the literature and as derived by using values from Table 1 in Eqn. 9 for two sets of samples from 'Radwaste' cores. The values obtained from the literature show very wide ranges of specific heat and diffusivity. Wide ranges of conductivity are expected, but even so, the ranges shown here for granite seem somewhat wide. Considering the general similarity of specific heats of minerals, shown in Table 1, the ranges of specific heats of rocks in Table 2 seem to be excessive. In particular, the first two lines for granites show specific heat for rock that is considerably higher than the specific heat of any major constituents. Such discrepancies between theoretical estimates based on mineral properties and direct measurement of rocks call into question both the principle of the method of estimation and the quality of the data available.

In the lines marked by '7m' in the reference column values of conductivity, density, specific heat and diffusivity are given as calculated by the geometric model from petrological and property data for 20 granodiorites from Atikokan and 10 granites from Pinawa. Petrological data are derived from Drury (1981) and the adopted mineral property data are shown in Table 3. The specific heat of plagioclase has been taken as the mean of the values for albite and anorthite. Properties for 'other minerals' are estimates, based on an approximate combination of the properties of the accessory minerals, including biotite, hornblende, epidote, chlorite, sphene, mafics and opaques.

In lines marked '7e', the experimental results for conductivity and density are given, these being the only properties measured so far.

Conclusions

1. The specific heat of some pure minerals is well known, including the major constituent minerals of granitic rocks. Other values needed to provide input data to all types of rock may be in the literature, but the sources are not known to the authors.
2. Predictions of diffusivity of granitic rocks from AECL Research areas may be made by a combination of measured conductivity and density and models of specific heat derived from literature data. These predictions do not agree well with the limited diffusivity data available.
3. The specific heat of some rocks, as derived from the literature, varies much more widely than is suggested by the specific heat of major constituent minerals, which is fairly uniform. Some of the published values must be regarded with suspicion, but we do not have an adequate knowledge of the relation of specific heat of a rock to that of its constituent minerals.
4. The validity of models for deriving specific heat and diffusivity from the data for constituent minerals has not been tested, but it is reasonable to assume that the diffusivity models will be equivalent to conductivity models and that specific heat is best modelled by simple addition by volume of the volumetric heat capacity.

5. The diffusivity of rocks is not adequately known for reliable prediction of diffusivity of the rock mass around any selected waste repository. This need could be met by a programme of measurement of either specific heat, followed by calculation of diffusivity, or of diffusivity directly. The authors favour the second alternative.

Bibliography

Drury, M.J., Estimation of the thermal conductivity of some crystalline rocks from their mineral composition. Geothermal Service of Canada Internal Report 80-9, 16pp., 1980.

__________, Thermal conductivity, density, porosity and mineralogy of core samples from Chalk R., Pinawa and Atikokan. Geothermal Service of Canada Internal Report 81-6, 13 pp., 1981.

Goranson, R.W., Heat capacity; heat of fusion. In - Handbook of physical constants, Ed. F. Birch, Geol. Soc. Am. Spec. Paper 36, 223-240, 1942.

Kappelmeyer, O. and Haenel, R., Geothermics. Gebrueder Borntraeger, Berlin, 1974.

Kelley, K.K., Contributions to the data on theoretical metallurgy, 12 - High temperature heat-content, heat-capacity, and entropy data for the elements and inorganic compounds. Bull. U.S. Bur. Mines 584, 232 pp., 1960.

Kieffer, S.W., Thermodynamics and lattice vibrations of minerals: 4 - Application to chain and sheet silicates and orthosilicates. Rev. Geophys. Space Phys. 18, 862-886, 1980.

Lindroth, D.P., Thermal diffusivity of six igneous rocks at elevated temperatures and reduced pressures. U.S. Bur. Mines, Rept. Invest. 7954, 33pp., 1974.

Lindroth, D.P. and Krawza, W.G., Heat content and specific heat of six rock types at temperatures to 1000°C. U.S. Bur. Mines, Rept. Invest. 7503, 24pp., 1971.

Moiseenko, O.I., Waermeleitfaehigkeit der Gesteine bei hohen Temperaturen. Freiberger Forsch, C238 Geophysik, 89-94, 1968.

Wenk, M.R. and Wenk, E., Physical constants of Alpine rocks. Schweizerische Mineralogische and Petrographische Mitteilungen 49, 343-357, 1969.

Table 1

Collected values of specific heat of minerals

	a	$b \times 10^3$	$c \times 10^{-5}$	C	Ref
Anorthite	$CaAl_2Si_2O_8$	MW = 278.22			
	950	226	231.3	757	1
	968.8	206.0	254.0	744	2
				759	3e
				720	3m
			mean	745 ± 8	
Albite	$NaAlSi_3O_8$	MW = 262.241			
	1018	187	268	772	1
	984.4	221.8	239.5	781	2
				783	3e
				770	3m
			mean	776 ± 3	
Orthoclase	$KAlSi_3O_8$	MW = 278.35			
	1043	124	351	685	1
	959.5	193.9	256.3	729	2
			mean	707 ± 16	
Quartz	SiO_2	MW = 60.09			
	757.4	607	168	749	1
	781.2	571	188	740	2
				742	3e
				734	3m
			mean	741 ± 3	
Calcite	$CaCO_3$	MW = 100.091			
	823	497	128.6	827	1
	1044	219	259	818	2
				832	3e
				801	3m
			mean	820 ± 6	
Dolomite	$CaMg(CO_3)_2$	MW = 184.422		930(a)	2
Halite	$NaCl$	MW = 58.448			
	773	300	0	862	1
	786	279	0	869	2
				865	3e
				852	3m
			mean	862 ± 3	
Sillimanite	Al_2SiO_5	MW = 162.05			
	1054	123	257	802	1
	1035	151.3	261.5	786	2
				757	3e
				738	3m
			mean	771 ± 12	

Table 1 Continued

	a	$b \times 10^3$	$c \times 10^{-5}$	C	Ref
Wollastonite	$CaSiO_3$	MW = 116.17			
	1054	74	269	726	1
	959.4	129.7	234.8	734	2
			mean	730 ± 3	
Diopside	$CaMg(SiO_3)_2$	MW = 216.58			
	1053	111	290	760	1
	1021.4	151.5	304.1	724	2
				769	3e
				769	3m
			mean	756 ± 9	
Pyroxene	$MgSiO_3$	MW = 100.41			
	973	336	233	811	1
	858	500	169	817	2
			mean	814 ± 2	
Amphibole	$MgSiO_3$	MW = 100.41			
	1067	183	281	805	1
	1023	227	245	815	2
			mean	810 ± 7	
Clinoenstatite	$MgSiO_3$	MW = 100.41			
	1023	198	262	787	2
				817	3e
				824	3m
			mean	809 ± 9	

References: 1 - Goranson, 1942; 2 - Kelley, 1960; 3 - Kieffer, 1980
e - experimental, m - model.

Table 2

Collected values of thermal properties of rocks

Rock Type	Conductivity W/mK	n	Density kg/m^3	n	Spec. Heat J/kgK	n	Diffusivity mm^2/s	n	Ref.
Granite	1.75 - 3.08	12	2500-2720	12	796-963	8	1.03-1.43	8	1
	1.67 - 2.83	13	2600-2650	13	879-1382	13	.50-1.51	13	2
			2600-2700	8	670-796	8	.68-1.20	8	3
					754 (mean)	6			4
					921	2			5
	2.90 - 3.29	10	2640-2660	10	735-746	10	1.49-1.65	10	7m
	2.89 - 3.53	10	2610-2640	10					7e
Rhyolite							.64	1	6
Granodiorite	1.64 - 2.33	9	2620-2760	9	837-1256	13	.50- .91	13	2
	2.84 - 3.21	20	2660-2670	20	744-749	20	1.43-1.61	20	7m
	3.07 - 3.59	20	2610-2660	20					7e
Gneiss	2.58 - 2.94	4	2700-2730	4	754-879		1.13-1.41	4	1
			2610--2950	55	461-921	55	.60-1.57	55	3
Pegmatites			2770-2630	3	670-837	3	.87-1.40	3	3
Gabbro							.92	1	6
Schists			2600-2860	16	670-1047	16	.78-1.80	16	3
Basalt							.67	1	6
Amphibolites			2790-3100	8	670-879		.61- .77	8	3
Ultrabasic			2720-3160	5	879-1005	5	.92-1.80	5	3
Dunite							1.34	1	6
Quartzite			2660	1	796	1			1
			2640	2	712-921	2	1.87-1.92	2	3
					921	1			5
					712	1			4

References: 1 - Kappelmeyer and Haenel, 1974; 2 -Moisseenko, 1968;
3 - Wenk and Wenk, 1969; 4- Birch, 1942; 5 - Lindroth and Krawza, 1971;
6 - Lindroth, 1974; 7 - this report

Table 3

Physical properties used in models

	Conductivity W/mK	Spec. Heat J/kgK	Density kg/m^3	Diffusivity mm^2/s
Quartz	7.7	741	2650	3.9
Plagioclase	2.0	760	2690	.98
Orthoclase	2.4	707	2560	1.3
Others	3.0	780	2820	1.4