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**REPORT**

**MRL-R-777**

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INTERMEDIATE FREQUENCY SOUND ABSORPTION IN SEAWATER:  
THE ROLE OF MAGNESIUM SULPHATE

Daniel J. Whelan

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INTERMEDIATE FREQUENCY SOUND ABSORPTION IN SEAWATER:  
THE ROLE OF MAGNESIUM SULPHATE

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Daniel J. Whelan

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ABSTRACT

↓  
The resonant absorption frequency,  $f_{RI}$ , and the excess absorption parameter,  $(\alpha)_{RI}$ , for 0.014 m  $MgSO_4$  in water at 4°C and 100 atmosphere pressure have been calculated and agree quite closely with those values defined by the Thorp equation for deep ocean sound channel absorption at intermediate frequencies.

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POSTAL ADDRESS: Chief Superintendent, Materials Research Laboratories  
P.O. Box 50, Ascot Vale, Victoria 3032, Australia

409014

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## DOCUMENT CONTROL DATA SHEET

Security classification of this page:

UNCLASSIFIED

1. DOCUMENT NUMBERS:		2. SECURITY CLASSIFICATION:	
a. AR Number:	AR-002-162	a. Complete document:	UNCLASSIFIED
b. Series & Number:	REPORT MRL-R-777	b. Title in isolation:	UNCLASSIFIED
c. Report Number:	MRL-R-777	c. Abstract in isolation:	UNCLASSIFIED
3. TITLE:			
INTERMEDIATE FREQUENCY SOUND ABSORPTION IN SEAWATER: THE ROLE OF MAGNESIUM SULPHATE			
4. PERSONAL AUTHOR(S):		5. DOCUMENT DATE:	
WHELAN, Daniel J.		JUNE, 1980	
		6. TYPE OF REPORT & PERIOD COVERED:	
7. CORPORATE AUTHOR(S):		8. REFERENCE NUMBERS:	
Materials Research Laboratories		a. Task: Marine Chemistry Research DST 78/150	
		b. Sponsoring Agency: Defence	
		9. COST CODE: 284420	
10. IMPRINT (Publishing establishment):		11. COMPUTER PROGRAMME(S):	
Materials Research Laboratories, P.O. Box 50, Ascot Vale, Vic.3032		(Title(s) and language(s)):	
JUNE, 1980			
12. RELEASE LIMITATIONS (of the document):			

Approved for Public Release

12-0. OVERSEAS:

N.O.

P.R.

1

A

B

C

D

E

13. ANNOUNCEMENT LIMITATIONS (of the information on this page):

No Limitation

14. DESCRIPTORS:

630	Acoustic absorption	645	Magnesium sulphate
	Underwater sound transmission		Sound attenuation
			SOFAR channel

15. COSATI CODES: 2001 0704 0810

16. ABSTRACT (if this is security classified, the announcement of this report will be similarly classified):

The resonant absorption frequency,  $f_{r1}$ , and the excess absorption parameter,  $(\alpha\lambda)_{r1}$ , for 0.014 m  $\text{MgSO}_4$  in water at 4°C and 100 atmosphere pressure have been calculated and agree quite closely with those values defined by the Thorp equation for deep ocean sound channel absorption at intermediate frequencies.

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## INTERMEDIATE FREQUENCY SOUND ABSORPTION IN SEAWATER:

### THE ROLE OF MAGNESIUM SULPHATE

#### 1. INTRODUCTION

In the early fifties, Wilson and Leonard [1] and Kurtze, Tamm and Kaiser [2] established that magnesium sulphate is primarily responsible for the absorption of sound in seawater over the frequency range 50-500 kHz and that the sound absorption curve at ambient conditions for 0.014 m  $\text{MgSO}_4$  in pure water is very similar to that from natural seawater. Subsequently Eigen and Tamm [3] proposed that this sound absorption is due to molecular relaxation arising from solvent separated  $\text{MgSO}_4$  ion pairs with varying degrees of hydration and this concept has been analysed kinetically in considerable detail [4-6]. It has also been found to be consistent with results from electrical conductance [7], from  $\text{H}^1$  nmr proton exchange [8] and from laser Raman spectroscopy [9].

In seawater (35% salinity), the averaged analytical concentration of  $\text{Mg}^{++}$  (free and associated) is 0.052 m and that of  $\text{SO}_4^{--}$  is 0.028 m [10]; hence, only portion of the total  $\text{Mg}^{++}$  and total  $\text{SO}_4^{--}$  present in seawater is involved in the sound absorption process [11]. This is hardly surprising as seawater can be regarded as a multi-electrolyte solution in which many ionic interactions occur [12].

In this report, it is intended to substantiate the role played by  $\text{MgSO}_4$  in acoustic sound absorption in seawater under real conditions by comparing laboratory measurements with those observed in deep ocean sound channel experiments, an analysis which does not appear to have been done before.

## 2. ACOUSTICAL ABSORPTION IN SEAWATER

The absorption of sound in seawater can be defined over the whole spectrum by a series of relaxation phenomena, each of which can be described mathematically [2,6] by a Debye relationship of the form :

$$\alpha_i = \kappa_i \frac{f_{ri} f^2}{f_{ri}^2 + f^2} \quad (1)$$

In this equation,  $\alpha_i$  is the individual sound absorption coefficient ( $\text{dB km}^{-1}$ ) with respect to the particular relaxation process,  $i$ , under consideration,

$f$  is the observing frequency, usually in kHz

$f_{ri}$  is the relaxation frequency of the medium under the conditions of measurement, and  $\kappa_i$ , a characteristic of the medium, is a measure of its chemical compressibility under the influence of the perturbing process, in units of ( $\text{dB km}^{-1} \text{kHz}^{-1}$ ).

When  $f = f_{ri}$ ,

$$\alpha = \alpha_{ri} = \frac{1}{2} \cdot \kappa_i f_{ri} \quad (2)$$

If  $v$  is the velocity of sound in the medium, in units of  $\text{km msec}^{-1}$ ,

$$v = f_{ri} \lambda_{ri} \quad (3)$$

where  $\lambda_{ri}$  is the wavelength of the acoustic wave at resonance, (km).

Thus, from (2) and (3)

$$\kappa_i = \frac{2(\alpha_{ri} \lambda_{ri})}{v} \quad (4)$$

whence, from (1)

$$\alpha_i = \frac{2 \alpha_{ri} \lambda_{ri}}{v} \cdot \frac{f_{ri} f^2}{f_{ri}^2 + f^2} \quad (5)$$

It is common to discuss oceanographic acoustical data both in terms of "the excess absorption per wavelength at the resonant frequency",  $(\alpha_{r1} \lambda_{r1})$ , which is also written as  $(\alpha\lambda)_{r1}$ , and in terms of  $f_{r1}$ , the resonant frequency.

In seawater, the principal absorption at low frequency (1-5 kHz) is attributed to borate and to magnesium-carbonate interactions [13-15] and that at high frequency (above 250 kHz) to the viscous relaxation of water [16,17]. It is over the intermediate range that absorption attributed to  $MgSO_4$  relaxation occurs but, to the author's knowledge, laboratory results have never been compared directly with field results.

### 3. INTERMEDIATE FREQUENCY ABSORPTION, $MgSO_4$

#### (a) Field Measurements

In 1967, Thorp presented a semi-empirical equation describing the low frequency and intermediate frequency sound absorption occurring in various deep ocean (SOFAR) sound channels in Northern Hemisphere waters [18,19], especially in the Atlantic Ocean. This equation summarised a wide body of previously isolated knowledge and is still the basis for current developmental work [20].

The Thorp term referring to intermediate frequency sound absorption is given by

$$\alpha_1 = \frac{44 f^2}{4100 + f^2} \quad \text{dB km}^{-1} \quad (6a)$$

where  $f$  is in kHz. This transforms to

$$\alpha_1 = 0.6875 \times \frac{64 f^2}{f^2 + 64^2} \quad (6b)$$

applying to deep ocean sound channel transmission at 4°C and 35 ‰ salinity.

If one assumes the speed of sound in the SOFAR channel is ca.  $1.48 \times 10^{-3}$  km msec<sup>-1</sup>, [21], then, using equations 1, 4, 6, one can calculate under these conditions

$$\begin{aligned} f_{r1} &= 64 \text{ kHz} \\ \text{and } (\alpha\lambda)_{r1} &= \frac{1}{2}(0.6875 \times 1.48 \times 10^{-3}) \text{ dB} \\ &= 5.09 \times 10^{-4} \text{ dB} \end{aligned}$$

(SOFAR channel, 4°C, North Atlantic)



(b) *Laboratory Measurements*

In the laboratory, Atkinson and Petrucci [4] made a detailed study of the acoustic absorption spectrum of magnesium sulphate in water and determined both the resonant absorption frequency,  $f_{ri}$ , and the excess absorption per wavelength,  $(\alpha\lambda)_{ri}$ , in pure water at 25°C and at various concentrations, (Table 1). From their work it appears that both these parameters are concentration dependent.

If both these dependencies are linear with concentration - and independently obtained evidence suggests that they are (2) - then one can calculate graphically from the data in Table 1, that, at effective concentration of 0.014 m  $MgSO_4$  (the concentration of  $MgSO_4$  in pure water which gives an absorption equivalent to that observed in seawater) and at 25°C,

$$(\alpha\lambda)_{ri} = 5.5_3 \times 10^{-4} \text{ dB (25°C, 1 atmos.)}$$

and

$$f_{ri} = 127 \text{ kHz (25°C, 1 atmos.)}$$

The laboratory measurements of Fisher and Simmons [13] and the field experiments of Bezdek [22,23] have shown that both the overall attenuation and the resonant frequency are pressure and temperature dependent to a marked degree.

(c) *Influence of Temperature and Pressure on  $f_{ri}$*

From laboratory data reported by Mellen, Browning and Simmons [15] on the temperature dependence of the relaxation frequency of  $MgSO_4$  at 0.014 m, the author has calculated that, over the range 2°-30°C and at atmospheric pressure,

$$f_{ri} = 1.229 \times 10^7 \exp(-3415/T) \quad (7)$$

where T is in °K, and  $f_{ri}$  is in kHz.

From this equation, it can be shown that

(i) at 25°C,  $f_r$  equals 131 kHz, a value very similar to that of Atkinson and Petrucci (127 kHz), and

(ii) at 4°C,  $f_r$  equals 55 kHz.

If one assumes that the same temperature dependence defined in eqn. 7 also applies to Atkinson and Petrucci's work, then their value of  $f_{ri}$  reduces to 51 kHz and the averaged value of these two extrapolations of laboratory data for 0.014 m  $MgSO_4$  solutions is 53 kHz (1 atm., 4°C).

In 1973, Bezdek [23] studied the variation of  $f_{ri}$  and  $\alpha_i$  with depth, in seawater, off the coast of Southern California. Although the observed relaxation frequencies which he reported were less than those observed from laboratory studies at atmospheric pressure (Table 2), he observed that the frequency of the  $MgSO_4$  relaxation reaction increased with depth and could be approximated by a linear relation,

$$f_{ri}(d) = f_{ri}(0) + 7.5 \times 10^{-3} d \quad (8)$$

where  $d$  is the depth of the ocean channel in metres and  $f_{ri}(d)$  is the relaxation frequency (in kHz) at this depth.

If one assumes that a similar pressure dependence applies in solutions of  $MgSO_4$  and that, on average, the depth of the deep axis sound channel occurs around 1000 metres [21], then

$$\begin{aligned} f_{ri}(1000) &= 53 + 7.5 \text{ kHz} \\ &= 60.5 \text{ kHz, say } 61 \text{ kHz,} \end{aligned}$$

where  $f_{ri}(0)$  is the average value of Atkinson and Petrucci's and Mellen, Browning and Simmons' data, based on our calculations. This figure is very similar to that determined semiempirically by Thorp, 64 kHz (equation 6).

The close agreement of these figures may be fortuitous or it may suggest that ionic strength effects and competing equilibria in seawater have only a small effect on the value of  $f_{ri}$  for magnesium sulphate.

(d) *Excess Absorption Parameter*  $(\alpha\lambda)_{ri}$

What is the effect of temperature and pressure on the excess absorption parameter,  $(\alpha\lambda)_{ri}$ ?

From Fisher's original work in the laboratory and from Bezdek's field work [20], attenuation is pressure dependent, following an approximate relation,

$$\alpha(d) = \alpha(0)(1 - 10^{-4} d) \quad (9)$$

where  $\alpha(d)$  is the sound absorption coefficient of 0.014 M  $MgSO_4$  at a depth,  $d$  (metre).

At a depth of 1000 m, this reduces to

$$\alpha(1000) = \alpha(0) \times 0.90$$

Millero and his co-workers [24] have established that the sound speed for 0.014 m MgSO<sub>4</sub> at 25°C and 1 atmosphere is very similar to that at 4°C and 100 atmosphere pressure, so that any change in  $(\alpha\lambda)_{ri}$  or  $(\alpha_r\lambda_r)_i$  will correspond to changes in  $\left(\frac{\alpha_r}{f_r}\right)_i$  with temperature and pressure.

At 25°C (1 atm.),  $f_{ri}$  is ca. 130 kHz, and at 4°C (100 atmos., 1000 m),  $f_{ri}$  is ca. 60 kHz. Hence,  $f_{ri}$  considerable change in  $(\alpha\lambda)_{ri}$  will occur by virtue of a change in  $f_{ri}$ , unless there is an accompanying change in  $\alpha_i$ .

Fisher and Simmons [13] have reported a relationship between temperature and pressure, based on experimental results in the laboratory, which in effect reduce to

$$\alpha_i (25^\circ\text{C}, 1 \text{ atm.}) = \frac{108 f^2}{27536 + f^2} \text{ dB km}^{-1} \quad (10)$$

and

$$\alpha_i (4^\circ\text{C}, 100 \text{ atm.}) = \frac{33 f^2}{5046 + f^2} \text{ dB km}^{-1} \quad (11)$$

The validity of using these equations out of context [13] has not been established but they are the best equations available for the purpose of this exercise.

Values of  $\alpha_{ri}$ ,  $\left(\frac{\alpha_r}{f_r}\right)_i$  and  $(\alpha\lambda)_{ri}$  based on calculations from these equations are given in Table 3.

The individual values of  $f_{ri}$  and  $(\alpha\lambda)_{ri}$  used by Fisher and Simmons in their equations are different from those calculated in this report but this is another issue. It is the ratio of the two values of  $(\alpha\lambda)_{ri}$  under the conditions described by Thorp (4°C, 100 atm., 35‰ salinity) which is of interest here.

This ratio is given by

$$\frac{(\alpha\lambda)_{ri} [25^\circ\text{C}, 1 \text{ atm.}, 130 \text{ kHz}]}{(\alpha\lambda)_{ri} [4^\circ\text{C}, 100 \text{ atm.}, 60 \text{ kHz}]} = \frac{4.68 \times 10^{-4}}{3.39 \times 10^{-4}} = 1.38$$

Hence, Atkinson and Petrucci's laboratory results are reduced from

$$(\alpha\lambda)_{r1} [25^\circ\text{C}, 1 \text{ atm.}, 0.014 \text{ m MgSO}_4] = 5.5_3 \times 10^{-4} \text{ dB}$$

by this factor, 1.38 to

$$(\alpha\lambda)_{r1} [4^\circ\text{C}, 100 \text{ atm.}, 0.014 \text{ m MgSO}_4] = 4.0_1 \times 10^{-4} \text{ dB}$$

which compares with the Thorp value of

$$(\alpha\lambda)_{r1} [\text{SOFAR}, 4^\circ\text{C}, 35 \text{ }^\circ/\text{oo salinity}] = 5.0_9 \times 10^{-4} \text{ dB}$$

In view of the many assumptions used to arrive at these comparisons and the inherent limitations in evaluating the experimental data both in the laboratory [25] and in the deep ocean [26], the agreement is surprisingly good. It confirms the commonly held belief that the intermediate frequency sound absorption in seawater is, in fact, dominated by  $\text{MgSO}_4$  interactions and not artifacts associated with it.

#### 4. SUMMARY

The resonant absorption frequency,  $f_{r1}$ , and the excess absorption parameter,  $(\alpha\lambda)_{r1}$ , as determined in the laboratory, for 0.014 m  $\text{MgSO}_4$  in water at 25°C have the values of ca. 130 kHz and  $5.5_3 \times 10^{-4}$  respectively. Both these parameters depend on temperature and pressure.

Under conditions found in typical deep ocean sound channel axes (4°C, 100 atm., 35<sup>o</sup>/<sub>oo</sub> salinity), it has been calculated that  $f_{r1}$  should change to ca. 60 kHz and  $(\alpha\lambda)_{r1}$  to  $4.0_1 \times 10^{-4}$  dB values which agree very closely with those actually observed in field experiments, namely

$$f_{r1} = 64 \text{ kHz}$$

and

$$(\alpha\lambda)_{r1} = 5.09 \times 10^{-4} \text{ dB,}$$

based on the Thorp equation.

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T A B L E 1

RELAXATION PARAMETERS IN AQUEOUS  $MgSO_4$  AT  $25^\circ C$ ,  
AT 1 ATMOSPHERE PRESSURE, FOLLOWING  
ATKINSON AND PETRUCCI, (REF. 4)

Conc. (M)	0.09889	0.1493	0.1965
$f_r$ (kHz)	133	137	140
$(\alpha\lambda)_r \times 10^4$ (Neper)	4.5	6.8	9.0
$(\alpha\lambda)_r \times 10^3$ (dB)	3.91	5.91	7.82

T A B L E 2

VARIATION OF RELAXATION FREQUENCY OF  $MgSO_4$   
IN SEAWATER, OFF SAN DIEGO, WITH DEPTH,  
FOLLOWING BEZDEK, (REF. 23)

Depth (metre)	Relaxation Frequency (kHz)
0	45
1000	52
2000	60



T A B L E 3

DEPENDENCE OF ACOUSTICAL VARIABLES ON TEMPERATURE AND PRESSURE  
AS CALCULATED BY FISHER-SIMMONS EQUATIONS (EQN. 10, 11)

$$\alpha_i (25^\circ\text{C}, 1 \text{ atm.}) = \frac{108 f^2}{27536 + f^2} \quad \text{dB km}^{-1}$$

$$\alpha_i (4^\circ\text{C}, 100 \text{ atm.}) = \frac{33 f^2}{5046 + f^2} \quad \text{dB km}^{-1}$$

Assume  $f_{ri}$  has values calculated from Ref. 4.

At  $25^\circ\text{C}$ , 1 atm. with  $f = f_{ri} = 130 \text{ kHz}$

$$\alpha_i = 41.07 \text{ dB km}^{-1}$$

$$\frac{\alpha_i}{f_{ri}} = 0.316 \text{ dB km}^{-1} \text{ kHz}^{-1}$$

$$(\alpha\lambda)_{ri} = 4.68 \times 10^{-4} \text{ dB}$$

At  $4^\circ\text{C}$ , 1000 atm. with  $f = f_{ri} = 60 \text{ kHz}$

$$\alpha_i = 13.74 \text{ dB km}^{-1}$$

$$\frac{\alpha_i}{f_{ri}} = 0.229 \text{ dB km}^{-1} \text{ kHz}^{-1}$$

$$(\alpha\lambda)_{ri} = 3.39 \times 10^{-4} \text{ dB}$$

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