Sodium chloride is widely used as an internal pressure standard in high pressure research. This paper discusses possible corrections needed in the calibration of this standard due to two independent effects, stress anisotropy and stress concentration, in pressure vessels. The first is due to the lack of a truly hydrostatic state of stress in solid state pressure vessels. The second is due to the difference in the compressibilities between the pressure transmitting substances (in this paper sodium chloride) and a stiffer test specimen. These two corrections are then combined and a total correction, as a function of measured pressure, is discussed for two systems presently in use. The predicted value of the combined effect is about 5-10% of the pressure.
INTRODUCTION

Jamieson first used sodium chloride as an internal pressure standard in x-ray studies on phosphorous\(^1\). He based his pressure scale on lattice parameter measurements in sodium chloride and the P-V data of Bridgman.\(^2\) Subsequently Decker\(^3\) proposed an equation of state for sodium chloride which was assumed to be good to about 30 GPa at which point a phase change occurs. By combining a measured lattice parameter, \(a\), with this theoretical equation of state (fitted to \(a_0\) and the bulk modulus at zero pressure, \(B_0\)), the pressure could be determined. As higher accuracy in the equation of state is attained, it becomes desirable to re-examine some of the assumptions generally made.

In high pressure research it is generally assumed that a hydrostatic state of stress is attained in a small region between the pistons of the vessel. Since the pressure transmitting materials used have low shear strengths and thus flow plastically at low pressures, this is thought to be a very good approximation particularly at higher pressures. It will be shown here that the magnitude of the correction for a material with a finite yield strength, though small, becomes important as higher accuracies are desired.

Another assumption, which on casual examination seems rather innocuous, is made when sodium chloride is used both as the pressure medium and the pressure gauge: it is assumed that the pressure in the sodium chloride standard (as seen by the x-rays) is the same as the pressure on the test specimens.
However, it has been previously noted experimentally by Jamieson and Olinger that stress concentrations exist around the test particles if these are elastically stiffer than the surrounding sodium chloride matrix.

Corrections for these two effects, stress anisotropy and stress concentration, can be calculated analytically if strain hardening in the sodium chloride is ignored. In this analysis we assume that the elastic constants and the yield strength depend linearly on the pressure. This seems sufficient for a first order correction for these effects.

STRESS ANISOTROPY

Here we consider a pellet of some polycrystalline material in an ideal pressure vessel as illustrated in Figure 1. The stresses of this configuration (in which there is no radial displacement) were analyzed in a previous paper. It was shown that the compression normal to given crystallographic planes in the sample disc is dependent on their orientation with respect to the axis of the pistons.

Consider diffraction from a plane (hkl) as shown in Figure 1. The entering x-ray beam is in the direction of piston motion. Measurement of the diffraction angle for this plane leads to the lattice parameter in a direction normal to the plane, i.e. the \( r' \) direction. From this we can obtain the strain in the \( r' \) direction and, from a known equation of state and assuming hydrostaticity, the apparent pressure, \( P_{r'} \), in the same direction.
It has been shown\(^6\) that the difference between the apparent pressure in the \(r'\) direction and the mean normal pressure (negative of the average of the three principal stresses) is given by

\[
\frac{P_{r'} - P_{nn}}{P_{nn}} = \left(1 + \nu(P_{nn})\right)\left(1 + \cos 2\alpha\right) - \frac{1}{3}\left(1 + \frac{E_{0}'}{E_{0}}\right)\sigma_{oo};
\]

(1)

here \(P_{r'}\) is the apparent pressure in the \(r'\) direction, \(P_{nn}\) is the mean normal pressure, \(\nu\) is Poisson's ratio (at pressure \(P_{nn}\)), \(E_{0}\) is the zero pressure Young's modulus and \(E_{0}'\) its pressure derivative, \(\sigma_{oo}\) is the zero pressure yield strength, and \(\alpha = 90^\circ - \theta\) (\(\theta\) is the Bragg angle.)

It should be noted that Young's modulus has been assumed to vary according to

\[
E = E_{0} + E_{0}' P_{nn}.
\]

(2)

In addition the pressure derivative of the yield strength has been replaced by \(\frac{E_{0}'}{E_{0}}\sigma_{oo}\).\(^7\) In the derivation of (1), Poisson's ratio was left as a general function of pressure, \(\nu(P)\). However in calculating an actual value for the apparent deviation from hydrostaticity \((P_{r'} - P_{nn})/P_{nn}\) at a given \(P_{nn}\), it is necessary to know \(\nu(P_{nn})\). It is of interest to note that a linear equation for \(\nu(P_{nn})\), such as (2) does not suffice because according to available data,\(^8\) this predicts \(\nu > \frac{1}{2}\) for most elastically compliant materials at pressures above about 15 GPa (150 kbars). Poisson's ratio for an isotropic medium must be less than one-half. We are therefore led to conclude that
v(P) varies much less rapidly with P than predicted by a linear relation. In the absence of any specific knowledge of how v varies with pressure, it has been assumed to be constant with respect to pressure; we have used two fixed values, one of these being $v = v_0$. The likely effect of using $v = v_0$ is to underestimate the deviation from hydrostaticity.

From Equation (1) we can calculate the ratio $P_{nn}/P_r$, using the Decker$^3$ equation of state for sodium chloride. Table 1 shows the elastic constants of NaCl used in the calculations.

Table 1 - Elastic Constants of NaCl

\[
\begin{align*}
\sigma_{00} &= 0.1 \text{ GPa}, 0.2 \text{ GPa} \\
E_0 &= 36.62 \text{ GPa} \\
E_0' &= 5.22 \\
v_0 &= 0.242
\end{align*}
\]

$E_0$, $E_0'$, and $v_0$ were calculated from single crystal values$^9$ according to the method of Hashin and Shtrikman.$^{10}$ The value of $\sigma_{00}$ of 0.1 GPa is consistent with that found by Aladag et al.$^{11}$ (for strains of 30% which we estimate are attained in pressing NaCl samples). Since this analysis ignores strain hardening, we have also calculated $P_{nn}/P_r$, versus $P_r$, for $\sigma_{00} = 0.2$ GPa in order to provide a possible upper limit for this effect. We have ignored creep and stress relaxation effects although such effects are well known in sodium chloride near room temperature and at very modest pressures (0.2 GPa).$^{12}$ Our reason for ignoring these effects is that they are controlled by
the diffusion rate of the slowest moving ion (chlorine in this case) and this process is retarded by pressures as has been shown in the case of LiBr$^{13}$ so that the rate will be slowed by several orders of magnitude at pressures of 10GPa or more.

Present experimental techniques$^{14,15}$, which are approximated in this analysis by an ideal pressure vessel configuration, use the first few Bragg diffraction lines in determining the apparent pressure in the sodium chloride ($P_r$). It was found sufficient here to use just the (200) reflections in calculating the anisotropy correction. (The correction depends on the reflections used only through the term $\cos2\alpha$, and the cosine function is close to minus one for all of the first three reflections, i.e., $2\alpha$ is close to 180°.) The results of the calculations are shown in Figure 2.

It should be noted that the corrections for the stress anisotropy calculated here were for a sample consisting only of sodium chloride. For samples with other materials mixed in with the sodium chloride the values for the elastic constants and the yield strength used in calculations should be those of the composite material. Thus if the added material is significantly stiffer than sodium chloride, the corrections will be greater. This becomes an increasingly important "second order" correction as the volume fraction of the stiffer material becomes larger. Second order corrections have not been calculated here since the necessary data for composite materials is not available. Finally, the substitution of $v_0$ for $v$ undoubtedly means that $v$ (and hence the ratio $(1+\nu)/(1-2\nu)$ in Equation (1) has been underestimated, perhaps by a factor as large as two or three. Until our knowledge of $\nu(P)$ is improved, there is little that we can do to improve this approximation. Thus Figure 2 also shows the results of
of calculations with the ratio \( \frac{1+v}{1-2v} \) increased by a factor of two.

STRESS CONCENTRATION

Jamieson and Olinger\textsuperscript{4} demonstrated the stress concentration effect for elastically stiffer niobium particles imbedded in a sodium chloride matrix. Their results were in qualitative agreement with Bobrowsky's\textsuperscript{16} treatment of elastically stressed spheres of a compliant matrix concentric with stiff compliant spherical inclusions. Bobrowsky found that the stresses in the matrix increase, i.e. are concentrated, towards the elastically stiffer inclusions. With such soft matrices, however, plastic flow begins at pressures which are very small in comparison with those of interest here. Thus to obtain corrections at high pressures, quantitative expressions were needed which would be applicable even after plastic flow in the softer matrix commences.

To accomplish this, a simple concentric sphere model is used. Consider the stiff material (assumed incompressible) to be in the form of a small sphere of radius \( a \) concentric with a larger sphere of the compliant material of radius \( b \). It is then assumed that such spheres fill all space in the sample disc. It is convenient to define a radius ratio \( K = \frac{b}{a} \). Thus \( \frac{1}{K} \) is the volume fraction of the stiff material in the sample to be pressurized.

Each composite sphere is treated individually, and has a common applied pressure of \( P_{ext} \) at the surface of the compliant spheres.
The stress concentration factor, \( \frac{P_{\text{int}}}{P_{\text{ext}}} \) (\( P_{\text{int}} \) is the pressure on the inclusion), is a constant until values for \( P_{\text{ext}} \) are high enough that the compliant matrix begins to flow plastically. It is noted that this plastic flow occurs first at the interface between the matrix and the inclusions, and this spherical plastic region expands from \( r = a \) (partially plastic case) to \( r = b \) (completely plastic case) as \( P_{\text{ext}} \) increases. The value of \( P_{\text{ext}} \) for which plastic flow begins is of the same order as the yield strength of the matrix (and not strongly dependent on \( K \)) while the value of \( P_{\text{ext}} \) necessary for the matrix to become completely plastic is highly dependent on the radius ratio \( K \). Once the matrix is completely plastic the applicable equation for the stress concentration is

\[
\frac{P_{\text{int}}}{P_{\text{ext}}} = K^n + (K^n - 1) \frac{E_o}{E_0 P_{\text{ext}}} \tag{3}
\]

Here \( n \) is the dimensionless quantity

\[
n = \frac{2E_o' \sigma_{\infty}}{E_o + 2 \frac{E_o}{3} \sigma_{\infty}} \tag{4}
\]

Derivations of the stress concentration for the completely elastic case, the partially plastic case, and the completely plastic case (Equation (3)) are described more fully elsewhere.\(^{17}\) The solution for the partially plastic case is not exact although it does give the appropriate expressions at the limits for the onset of yielding and for reaching the fully plastic state. Figure 3. shows the stress concentration for all three cases where the compliant matrix
is sodium chloride and \( K = 2 \).

In the above analysis strain hardening has been ignored as it was for the stress anisotropy effect. Including strain hardening effects would tend to increase the stress concentration factor. Another assumption made was that the stiff material was incompressible. This assumption is justified if its bulk modulus is many times greater than that of the compliant matrix. This is in fact the case for the iron inclusions to be discussed later. The isothermal bulk moduli for sodium chloride and iron are 23.7 and 173 respectively.

The present analysis is based on the assumption that the inclusions are spheres. In the actual case to be considered next, the inclusions are not spheres.

**COMBINED EFFECT**

We now wish to combine the above two effects. It would seem that the stress concentration would cause a broadening of the diffraction lines in the x-ray pressure determination because of the pressure gradient across the matrix. This would not be observed since most of the x-rays are diffracted from material in a region near the surface of the spheres (where most of the material is located); quantitative calculations by the authors show this to be true. We can relate \( P_{nn} \) to \( P_{ext} \) by

\[
P_{nn} = \frac{(3P_{ext} - 2\sigma_{oo})E_o}{(3E_o - 2E_o \sigma_{oo})}.
\]

\[ \text{(5)} \]
Thus we can find values for the ratio $P_{\text{int}}/P_r'$. Figure 4 shows this combined effect for several values of $K$ versus the measured pressure, $P_r'$.

In the study by Mao, et al.\textsuperscript{18} on iron, a volume fraction for the iron of about one-half was used.\textsuperscript{19} This corresponds to a radius ratio of $K = 1.26$. Figure 5 shows a plot of $P_{\text{int}}/P_r'$ versus $P_r'$ for two values of the yield strength, $\sigma_{oo} = 0.1\text{GPa}$ and $\sigma_{oo} = 0.2\text{GPa}$. In the ruby fluorescence study of Piermarini, et al.\textsuperscript{15}, a ruby volume fraction of $1/10$ ($K = 2.15$) was mixed in a 4:1 mixture of methanol and ethanol. The mixture of methanol and ethanol freezes as a glass at about $10\text{GPa}$\textsuperscript{20}, but there is no experimental data for the flow stress of such a glass which we can use to estimate the magnitudes of either effect.

CONCLUSIONS

It is of interest to note that the predicted combination of the stress anisotropy and the stress concentration factors, while not negligible, was not extremely large either, being in the neighborhood of only 5% at $30\text{GPa}$ for sodium chloride.

It should be noticed that the dependence of the two separate effects on $K$ are in the opposite direction, i.e. although decreasing $K$ decreases the stress concentration factor, it will increase the composite yield strength and thus the stress anisotropy factor. Thus some optimal $K$ should be chosen to minimize the effects.
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2. Stress Anisotropy effect for molybdenum Kα x-rays. a) $\sigma_{oo} = 0.1$ GPa and $\nu = \nu_0 = 0.242$. b) $\sigma_{oo} = 0.1$ GPa and $\nu = 0.359$ or $\sigma_{oo} = 0.2$ GPa and $\nu = \nu_0$. c) $\sigma_{oo} = 0.2$ GPa and $\nu = 0.359$.

3. Stress Concentration effect for $K = 2$, $\sigma_{oo} = 0.1$ GPa, and $\nu = \nu_0$. a) Low external pressure. b) High external pressure. The onset of yielding in the NaCl matrix is indicated by a single asterisk, while the beginning of the fully plastic condition is indicated by a double asterisk.

4. Combined effect for $K = 1.25, 1.5, 2.0$, and $3.0$; $\sigma_{oo} = 0.1$ GPa, and $\nu = \nu_0$.

5. Combined effect for $K = 1.26$. a) $\sigma_{oo} = 0.1$ GPa and $\nu = \nu_0$. b) $\sigma_{oo} = 0.1$ GPa and $\nu = 0.359$. c) $\sigma_{oo} = 0.2$ GPa and $\nu = \nu_0$. d) $\sigma_{oo} = 0.2$ GPa and $\nu = 0.359$. 
Fig. 3
Fig. 3
Fig. 5