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Thermal expansion and conductivity of magnetite flakes taken from the Oconee-2 steam generator

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Flakes consisting primarily of iron oxides (magnetite) have been discovered in the spaces between tubes and support plates in steam generators, increasing flow resistance and causing abnormal increases in water levels. To aid in the determination of the effects of tube scale on steam generators, Duke Power Company and MPR Associates, Inc. arranged for the author to measure the thermal expansion and thermal conductivity of tube scale specimens from the steam generator of the Oconee-2 pressurized water reactor. The study measured the thermal expansion of the flakes directly, using miniaturized specimens, rather than deriving these data from X-ray powder diffractometry as in past studies.

The flakes are composed of multiple layers, each of which exhibits different thermal behaviour. Thermal expansion was higher than that for Fe_3O_4. The average thermal conductivity for two- and three-layered flakes is 0.026 J sec^{-1} cm^{-1} ° C^{-1}. The thermal conductivity for a single-layered flake is 0.060 J sec^{-1} cm^{-1} ° C^{-1}.

1. Introduction

Small flakes which consist primarily of iron oxide (magnetite) have been discovered in the spaces between the tubes and support plates in the steam generator of the Oconee-2 plant. These flakes are believed to cause significant increases in flow resistance, which in turn cause abnormal increases in steam generator water level.

It is necessary to measure the physical properties of the tube scale so that the maximum number of flakes can be loosened before hydrodynamic cleaning (water slap). There are several preconditioning options, including prewetting, predrying, or thermal cycling of the steam-generator tubes. Once the thermal properties of the tube scale are determined, the best method of preconditioning can be chosen. Understanding the thermal properties of the scale would also be beneficial for optimizing the water slap technique itself. Several procedures and models for calculating the effects of tube scale on steam-generator performance are given in [1]. The author used patented miniature specimen techniques to measure important specimen properties such as thermal expansion, thermal conductivity and curling [2]. Studies of the fracture stress, elastic modulus and swelling of the Oconee-2 flake specimens are reported by Manahan [3].

2. Metallography, chemistry and specimen preparation

2.1. Metallography

Sludge from the generator was sorted and the largest flakes were removed for metallographic investigation and specimen preparation. Metallographic studies were conducted to investigate the microstructure of the flakes, and to determine whether anisotropy occurs in the plane normal to the tube radius. It was discovered that the flakes are reasonably isotropic and are composed of multiple layers. The average grain size near the centre of the cross section for three-layered flakes was found to be 0.005 mm. Grains near the outside diameter (OD) surface as large as 0.013 mm were observed. The metallographic tests and results – and their significance to the physical behaviour of the flakes – are described in full by Manahan [3].

2.2. Chemistry

Chemical and physical analysis of the sludge flakes was performed by Combustion Engineering (Windsor) and by Duke Power Company [4, 5]. The flakes studied were found to be nearly identical in chemical composition, iron magnetite being the major component. The concentration ranged from 68 to 70 wt % iron. All other elements had concentrations < 1 wt % [4]. A more detailed discussion of the physical and chemical make-up of the flakes appears in [3].

2.3. Specimen preparation

The sorted flakes were found to be irregular in shape with typical dimensions in the axial direction (i.e. parallel to the tube axis) of 3.81 to 5.08 mm, along the circumferential direction of about 2.54 mm, and from 0.1 to 0.2 mm in thickness.

The flakes were machined into thin, straight beams for determination of thermal expansion, thermal conductivity, and curling. The length dimension was

*The work was performed during employment at Battelle.

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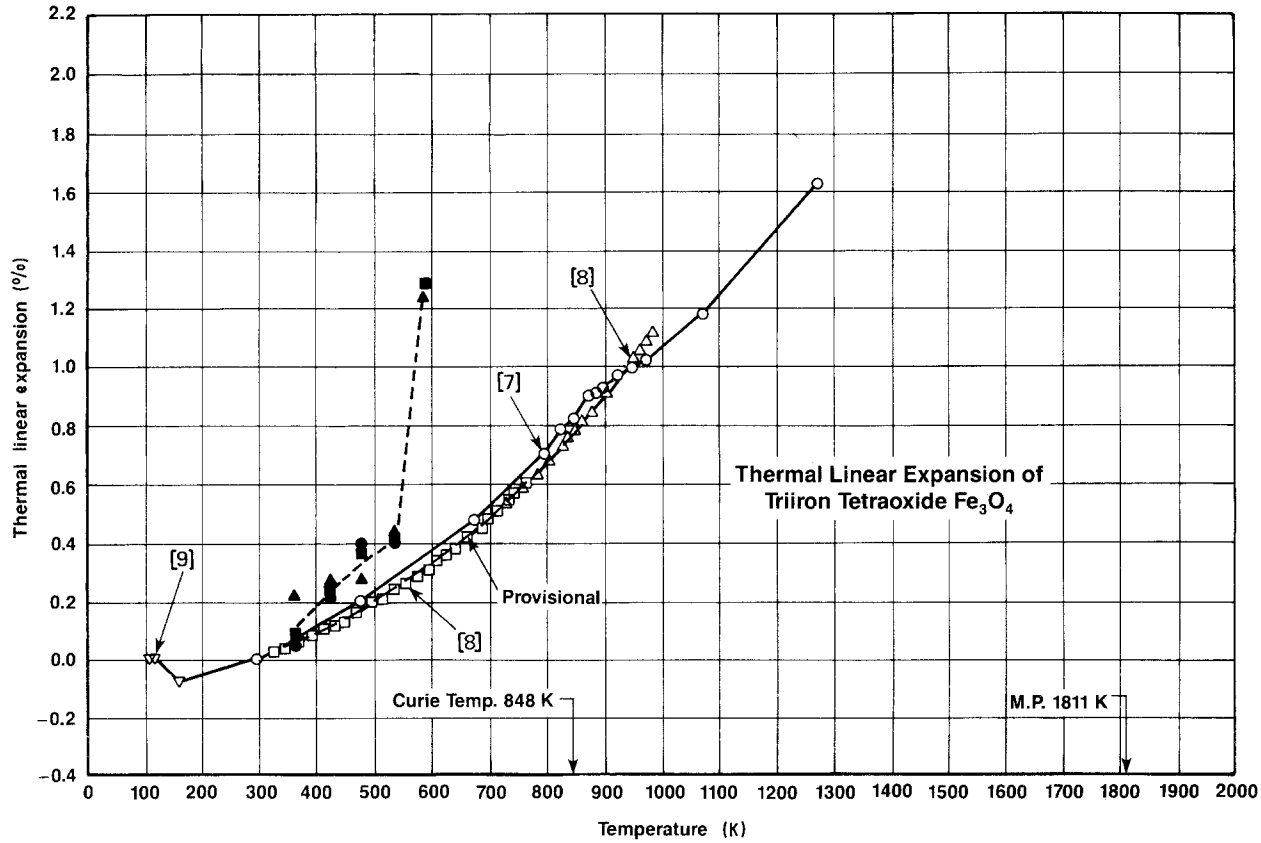

Figure 1 Comparison of Oconee miniature flake thermal expansion data with Fe_3O_4 data (from ref. 6). Specimens ▲, A; ●, G; ■, H; ----, fit to minature flake data.

parallel to the tube axis. The specimens were nominally 5.08 mm long, and were machined to a nominal width of 1.27 mm. Inside diameter (ID) and OD surfaces were not polished prior to testing since the goal was to determine the thermal properties of the sludge as it is in the steam generator environment. Therefore, care was exercised to maintain these surfaces in the as-received condition.

3. Methods and results

3.1. Thermal expansion

Thermal expansion measurements were made optically using a microscope with a precision x–y stage attached to a digital micrometer. The system has been designed so that backlash is essentially zero. The stage was calibrated so that the measurement uncertainty is much lower than the uncertainty in cross-hair placement.

The linear thermal expansion data for the Oconee flakes are presented in Table I and the data are compared with Touloukian *et al's* data [6] for Fe_3O_4 in Fig. 1. The mean coefficient of linear expansion over several temperature ranges is provided in Table II, while Table III provides the instantaneous coefficient of linear expansion at several temperatures. During the testing, nine readings were taken for length measurements at each temperature and these measurements were averaged. The average standard deviation for the data was consistently ~0.00328 mm.

The number of layers does not appear to correlate with thermal expansion response. The data at 316° C show a dramatic increase in the expansion coefficient. One possible explanation is a phase change. Additional work is necessary to explain this phenomenon. As described below, the thermal expansion data are likely to be a lower-bound estimate since specimen curling was observed.

3.2. Specimen curling measurements

During the thermal expansion experiments, some of the flakes appeared to curl on heating. When traversing the specimen, the microscope would occasionally need to be refocused, and some measurements indicated that the specimen was shortening. The apparatus that

TABLE I Linear thermal expansion data for Oconee miniature flake specimens

Specimen identification	Number of layers	Thickness (mm)	$\Delta L/L_0$ (%)*				
			RT 93° C	RT 149° C	RT 204° C	RT 260° C	RT316° C
A	3	0.213	0.22079	0.28912	0.28912	0.43631	1.24060
G	2	0.090	0.04392	0.21230	0.40264	0.40264	1.28111
H	1	0.194	0.09771	0.23451	0.37131	0.41040	1.28330
Average for flakes A, G, and H	–	–	0.12081	0.24531	0.35436	0.41645	1.26834
Ref. 6 data for Fe_3O_4	–	–	0.067	0.121	0.182	0.251	0.325

*L_0 is referenced to room temperature, 21° C.

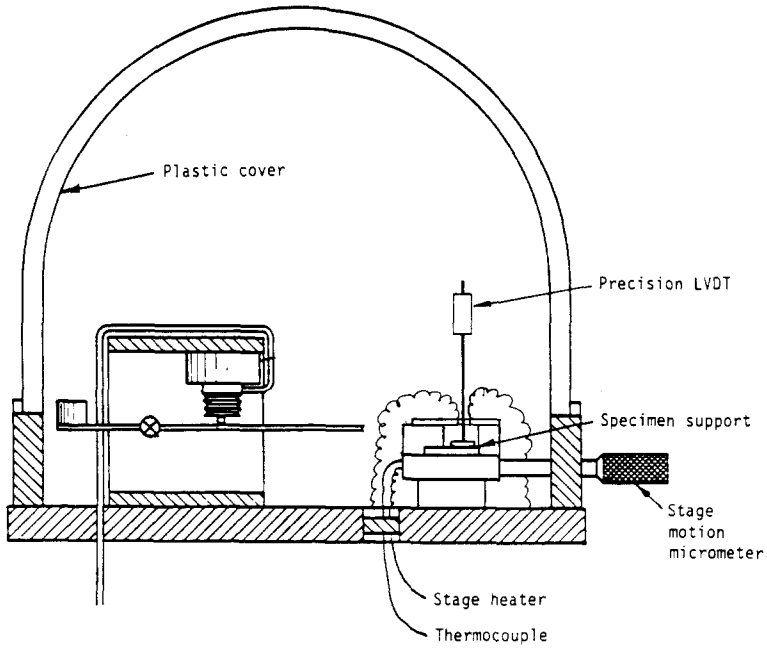

Figure 2 Schematic drawing of specimen curling apparatus.

had been used for the bend testing [3] was modified for curling measurements (Fig. 2). A quartz support plate was placed in the bend fixture, and the specimen rested on this surface with the flake OD surface (relative to the original tube) facing up. A glass slide with a hole cut near the centre was supported above the specimen and a precision linear variable-differential transducer (LVDT) rested near the centre of the specimen and passed through the hole in the glass plate. Thermal insulation was carefully placed around the specimen and LVDT.

The system was calibrated with the LVDT resting on the quartz base to determine the thermal expansion characteristics of the system. The specimens were then placed in the fixture and measurements were made. The time dependence of the temperature and displacement were recorded and stored on computer. Measurements were taken with one edge of the specimen fixed and without restraint. Since the weight of the LVDT core is approximately 1 g, the deflection measurements reported are lower-bound estimates. In order to measure the unrestrained flake curling, more elaborate optical deflection measurements would be necessary.

The results of the specimen curling measurements are given in Table IV. The first specimen tested, Specimen C, had one edge restrained since the direction of flake curling was unknown. The OD surface of the flakes deflect radially outward as referenced back to the in-service tube. The average minimum deflection in this direction is 0.307 mm.

The curling appears to be negligible up to ~204° C. Above this temperature, curling may be expected to have an important effect on the thermal expansion data. To obtain accurate thermal expansion data above 204° C, optical measurement of the flake curling would be necessary; these data could be used to develop a correction factor for the thermal expansion measurements. An estimate of the minimum effect can be made by assuming the flakes are initially flat and displace 0.038 mm at the centre. Assuming a flake length of 2.5 mm, the projected length of the flake on the specimen support surface would be 1.2695 mm, or approximately 57.15×10^{-5} mm shorter during a thermal expansion measurement. This would result in an underprediction of ~2.5% of the thermal expansion deflection. If the curling deflection were about twice that measured, 0.08 mm, the underprediction

TABLE II Mean coefficient of linear thermal expansion for Oconee miniature flake specimens

Specimen identification	Mean expansion coefficient α ($^\circ C^{-1} \times 10^{-5}$)				
	RT 93° C	RT 149° C	RT 204° C	RT 260° C	RT 316° C
Average for flakes A, G, and H	1.68	1.99	1.94	1.74	4.30
Ref. 6 data for Fe_3O_4	0.92	0.94	0.99	1.05	1.10

TABLE III Instantaneous coefficient of linear thermal expansion for Oconee miniature flake specimens

Specimen identification	Expansion coefficient α ($^\circ C^{-1} \times 10^{-5}$)							
	57° C	121° C	149° C	177° C	204° C	232° C	260° C	288° C
Average for flakes A, G, and H	1.68	2.22	2.10	1.98	1.54	1.11	10.88	15.21
Ref. 6 data for Fe_3O_4	0.92	0.84	1.04	1.11	1.17	1.23	1.28	1.32

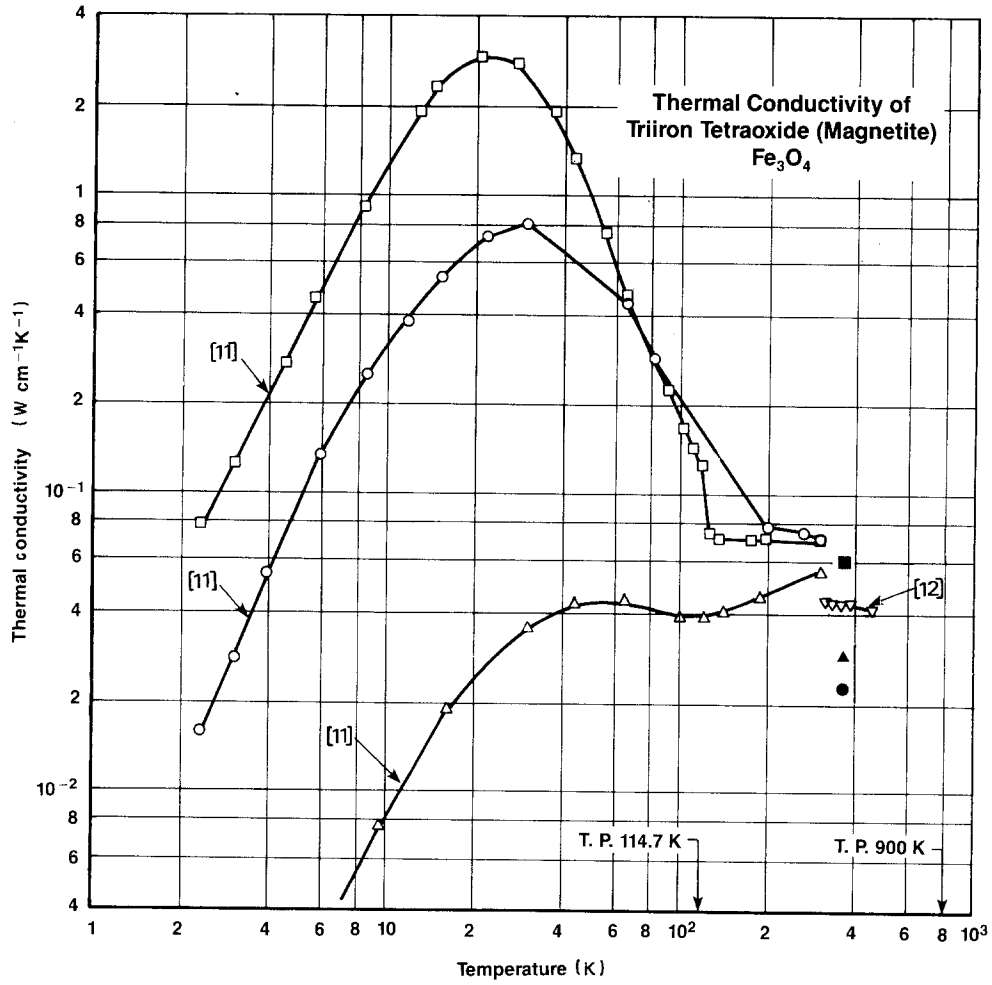

Figure 3 Comparison of Oconee miniature flake thermal conductivity data with Fe_3O_4 data (from ref. 10). Specimens ▲, B; ●, G; ■, H.

error for thermal expansion at 288° C would be 10%. If the curling deflection were five times that measured, the thermal expansion underprediction at 288° C would be 50%.

3.3. Thermal conductivity

The thermal conductivity was determined from measurements of laser diffusivity, heat capacity, and density. Thermal conductivity values were calculated from the relation

$$\lambda = C_p \varrho \alpha$$

where λ = thermal conductivity ($J\,sec^{-1}\,cm^{-1}\,°C^{-1}$), C_p = heat capacity at constant pressure ($J\,g^{-1}\,°C^{-1}$), ϱ = density ($g\,cm^{-3}$), and α = thermal diffusivity ($cm^2\,h^{-1}$). A total of three specimens (one, two and three layers) were tested.

The heat capacity was measured using differential scanning calorimetry (DSC). The density was determined from the mass and volume of each specimen and the thermal diffusivity was determined using the laser-flash diffusivity technique. The thermal response time for these samples is about the same duration as the laser pulse (2 m sec). This makes precise measurement of the thermal diffusivity difficult because it is necessary to deconvolute the sample signal from the laser pulse. A much better measurement could be obtained from a specimen which is a factor of 10 thicker than the Oconee flakes. Therefore the uncertainty in data reported is about ± 100% for specimens B and G and ± 50% for specimen H.

The thermal conductivity data are reported in Table V and compared with Touloukian *et al's* data [10] in Fig. 3. The one- and two-layered specimens had com-

TABLE IV Minimum specimen curling deflection

	Deflection measurement with LVDT on quartz base (mm)		Deflection measurement with LVDT on specimen (mm)		
	Run 1	Run 2	Specimen C‡ (Edge restrained)	Specimen B (No edge restraint)	Specimen F (No edge restraint)
Minimum deflection	0.1435	0.1397	0.1448*	0.1824*	0.1626*
Average	0.1417		0.1448	0.1725	
Average minimum deflection	(-)	(-)	~0	0.037	

*These data are considered to be minimum deflections since the LVDT rested on the specimen. The LVDT was placed near the centre of the specimen.
‡One edge of the specimen was restrained during the test.

TABLE V Oconee flake thermal conductivity data

Specimen identification	Number of layers	mass ($kg \times 10^{-6}$)	Thickness (mm)	Density ($g\,cm^{-3}$)	Thermal diffusivity, ($cm^2\,h^{-1}$)	Heat capacity, ($J\,g^{-1}\,°C^{-1}$)	Thermal conductivity, ($J\,sec^{-1}\,cm^{-1}\,°C^{-1}$)
B	3	8.573	0.14	3.128	50.400	0.63	0.028
G	2	4.690	0.09	3.294	39.600	0.63	0.023
H	1	10.510	0.19	3.598	93.600	0.63	0.06

parable conductivities that were approximately a factor of two below the single-layered specimen. These data are consistent with the data reported by Goodstine [13]. Goodstine's data ranged from 0.021 to $0.062\,J\,sec^{-1}\,cm^{-1}\,°C^{-1}$, and the variation was attributed to the structure of the scale. The data reported by Goodstine [13] were obtained by imposing a heat flux on a tube sample with flowing water and calculating the overall heat-transfer coefficient. Goodstine associated higher thermal conductivity with the highest porosity scale. Our tests, which were conducted in a vacuum, suggest the converse. The differences may be due to the test environment or test techniques. A convective component of the thermal conductivity was not present in Goodstine's tests, but is in the Battelle tests. Water would tend to fill in the porous region of the flakes and increase the conductivity.

4. Discussion

The thermal expansion of the tube scale was found to be significantly higher than that for pure Fe_3O_4 as reported by Touloukian *et al.* [6]. The specimens were observed to curl on heating. The curling appears to be small up to ~204° C. Thermal expansion measurements above ~204° C should be corrected for curling. The curling data reported represent the minimum deflection due to curling since the weight of the LVDT core, which rested on the specimen, would tend to flatten the specimen. Optical measurement techniques would be required in the future precisely to measure the curling deflection. The average thermal conductivity for two- and three-layered flakes is $0.026\,J\,sec^{-1}\,cm^{-1}\,°C^{-1}$. The thermal conductivity for a single-layered flake is $0.060\,J\,sec^{-1}\,cm^{-1}\,°C^{-1}$.

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