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Technical Report SL-93-4
April 1993

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Length Change and Strength Development of Candidate Cement-Based Sealing Mixtures for the WIPP

by *Toy S. Poole, Lillian D. Wakeley*
Structures Laboratory

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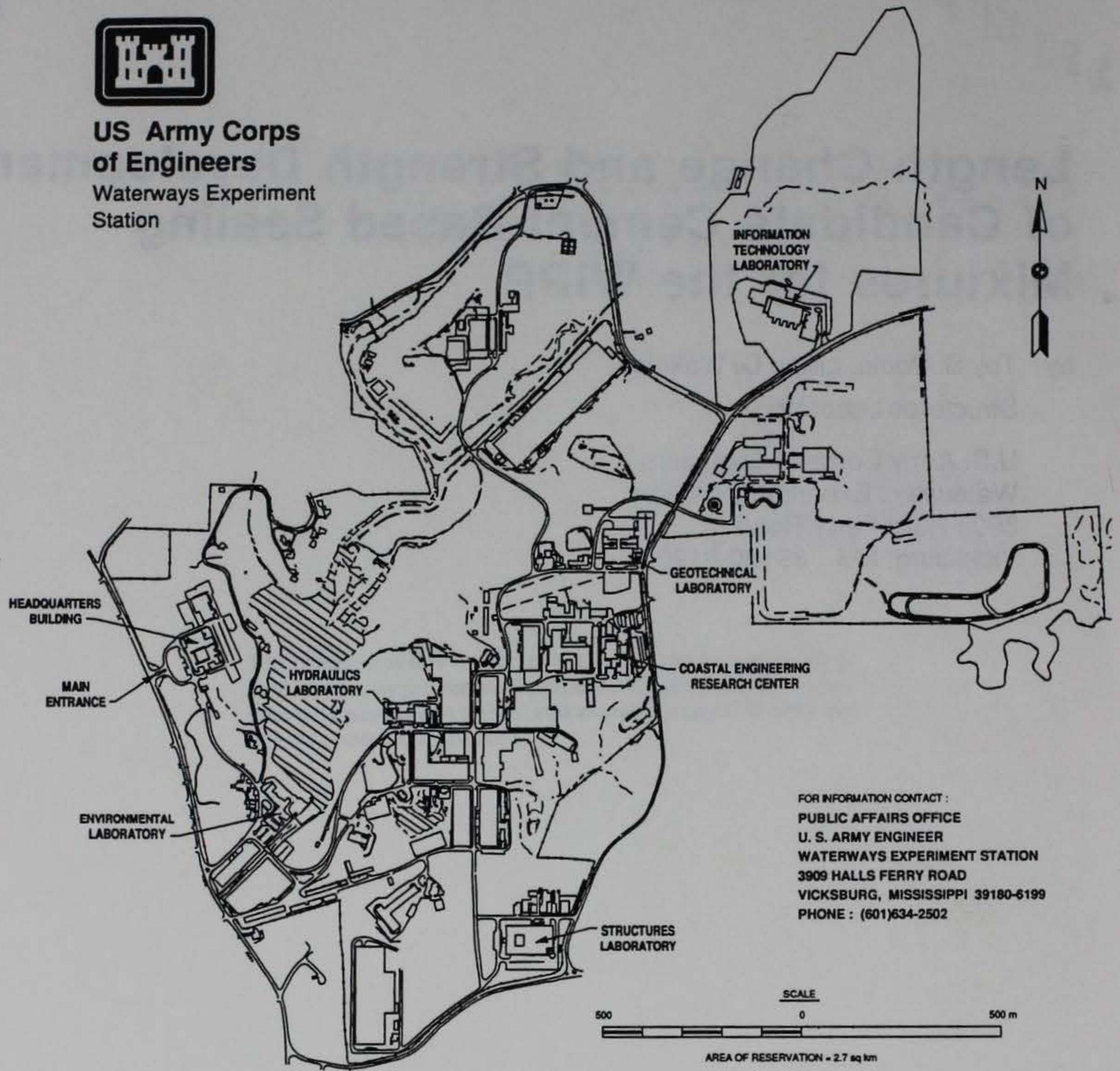
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Preface

This work was performed for Sandia National Laboratories (SNL), supported by the U.S. Department of Energy, under contract DE-AC04-76DP00789. The performing agency was the Concrete Technology Division (CTD), Structures Laboratory (SL), U.S. Army Engineer Waterways Experiment Station (WES), under SNL Document Number AA 2030. Dr. Lillian D. Wakeley, WES, was Principal Investigator. Dr. E. J. Nowak was Project Manager for SNL, Department 6121, of which Dr. Joe Tillerson is Manager.

Laboratory studies were accomplished in CTD during May through December, 1990, with direct guidance from Dr. Lillian D. Wakeley, Engineering Sciences Branch. The project plan was RPP 90-8 and RPP 90-08B. Dr. Toy S. Poole contributed to the planning of the project, analyzed the data, and wrote the report with assistance from Dr. Wakeley. Messrs. John Cook, Charles White, and Pete Burkes executed the technical work.

This project was accomplished under the general supervision of Mr. Bryant Mather, Director, SL; Mr. James T. Ballard, Assistant Director, SL; Mr. Kenneth L. Saucier, Chief, CTD. Dr. Wakeley was the principal investigator.

At the time of publication of this report, Director of WES was Dr. Robert W. Whalin. Commander was COL Leonard G. Hassell, EN.

1 Introduction

The purpose of some of the research at the Waterways Experiment Station (WES) in support of materials development for Sandia National Laboratories (SNL) and the Waste Isolation Pilot Plant (WIPP) was to describe quantitatively how placing and early-age properties of candidate grouts and concretes are affected by temperature, humidity, and properties of component materials. Previous work had investigated the effect of changing cement and pozzolan sources on length-change and early strength development (Buck et al. 1983). Changing cement source was found to have some effect on early length change, but later-age length change tended to converge on a common value. Type K cement-based mixtures expanded more than Class H oil-well cement-based mixtures. Changing pozzolan source appeared to have a strong effect on expansion. Changes in w/c also appeared to be important.

The effects of temperature and relative humidity have not been systematically investigated. Previous work on expansive behavior reported numerous instances when expansion mechanisms apparently failed. These events were attributed to poor sealing of specimens soon after casting, which allowed them to dry and consequently shrink. Companion specimens stored in water or in fog expanded. Clearly moisture availability is important, but the effect has not been quantified.

2 Mixtures, Materials, and Methods

In the work reported here, the length change and strength gain behavior of two expansive mixtures was investigated at several temperatures and relative humidities. One of the mixtures was a mortar equivalent of BCT-1-FF (Gulick and Wakeley 1989). This expansive grout has been the object of many previous studies of candidate sealing materials. The other mixture was based on a Type K expansive cement. Experimental conditions were selected to cover the probable range of temperatures and relative humidities to be expected in placing and early curing of concrete at the WIPP. Neither mixture contained sodium chloride as a component. Mixing proportions had been selected during a period of research on freshwater grouts, the use of which was anticipated in non-halide rock units at the WIPP.

Materials were as follows.

Material	Applicable Specification	CTD Ref. Number
Type K expansive cement	ASTM C 845	WIPP-1 RC-1
Class H oil-well cement	API 210	WIPP-1 RC-2
Class C fly ash	ASTM C 618	LMK-4 AD-4
High-range water reducer (HRWR)	ASTM C 494	
Standard graded sand	ASTM C 778	Lab stock
Deionized water	ASTM D 1193	Lab stock
Plaster	ASTM C 28	WIPP-1 RC-3

The Type K mixture contained fly ash (35 percent by absolute volume of cement), fine aggregate (sand), water, and a high-range water reducer (HRWR). The ratio of water to cement + fly ash (w/cfa) was 0.30 by mass. The ratio of cement + fly ash to sand was 0.5. The HRWR dosage was adjusted to give the mortar a flow of 110 ± 5 , according to ASTM C 109-90 (ASTM 1990a). The BCT-1-FF-like mixture was proportioned like the

Type K mixture except Class H oil-well cement and plaster (10 percent by mass of cement) were substituted for the Type K cement.

Restrained-expansion mortar bars (2 by 2 by 10 in.) were fabricated and measured according to ASTM C 806-87 through paragraph 11.3 (ASTM 1990b). Mortars were mixed and bars fabricated at 23 °C and stored in molds in a moist cabinet for 24 hours at the same temperature. They were then demolded and placed in the experimental temperature-humidity condition for 24 hours. Initial gage length was recorded at the end of this 48-hour period, so initial change in length was first measured at 3 days. Subsequent length-change measurements were taken daily, usually, to 7 days, and then weekly until the bars appeared to have reached length stability. Each datum in Tables 1 and 2 represents the mean length change of two bars, which were fabricated from the same batch. Some mixtures were duplicated but time and equipment constraints prevented full duplication of tests (total number of specimens: 60).

Mortar cubes (2-in.) were fabricated according to ASTM C 109 from the same batches from which the restrained bars were made. Cubes from all mixtures were tested for compressive strength at 3, 7, 14, and 21 days. Data from later ages also were collected when bar measurements were extended beyond 21 days. Two cubes were broken per mixture for most test ages shown in Tables 3 and 4 (total number of specimens: 330).

Temperature conditions were 23 °C, 30 °C, and 38 °C. Some mixtures were also tested at 50 °C. Relative humidity (RH) conditions were 50 percent, 75 percent, and 100 percent. A moist cabinet conforming to ASTM C 511 (ASTM 1990c) was used for the 23 °C, 100 percent RH condition. Two variably-adjustable environmental cabinets (Tenny Model 14, Standard International Systems Model RB/5) were used for the other conditions. Relative humidity conditions were verified by measurement with a wet-dry bulb thermometer.

Table 1 Length-Change Data, Class H Cement Mixtures				
Age (days)	23 °C	30 °C	38 °C	50 °C
100% Relative Humidity				
2	0.015			
3	0.020	0.005	-0.003	-0.017
4	0.027	0.006	-0.018	-0.014
5	0.037	0.002		
7	0.046	-0.015	-0.018	-0.029
14	0.064	-0.005	-0.017	-0.018
21	0.065	-0.004	-0.017	-0.016
28	0.067		-0.014	-0.015
37	0.066		-0.016	-0.018
75% Relative Humidity				
3	-0.001	0.002	-0.061	
4	-0.011	-0.004	-0.022	
5	-0.007	-0.008		
6	-0.008	-0.012		
7	-0.0184	-0.016	-0.030	
14	-0.026	-0.023	-0.034	
21	-0.030	-0.026	-0.037	
28			-0.035	
37			-0.034	
50% Relative Humidity				
3	-0.005	-0.010	-0.020	
4	-0.015	-0.022	-0.032	
5	-0.019	-0.030	-0.037	
6	-0.030	-0.039		
7	-0.035	-0.046	-0.046	
14	-0.053	-0.054	-0.051	
21	-0.052	-0.057	-0.050	
28			-0.048	
37			-0.048	

Table 2
Length-Change Data, Type K Cement Mixtures

Age (days)	23 °C	30 °C	38 °C	50 °C
100% Relative Humidity				
3	0.003	0.000	0.002	-0.011
4	0.004	-0.002	0.007	-0.004
5	0.006	-0.002		
7	0.010	-0.003	-0.004	-0.018
14	0.013	-0.002	-0.005	-0.010
21	0.015	-0.001	-0.005	-0.009
28	0.016		-0.002	-0.006
37	0.016		-0.002	-0.006
75% Relative Humidity				
3	-0.004	-0.002	-0.008	
4	-0.014	-0.006		
5	-0.012	-0.007		
6	-0.012	-0.008	-0.023	
7	-0.018	-0.008	-0.022	
14	-0.021	-0.016	-0.021	
21	-0.024	-0.019	-0.028	
28			-0.023	
49			-0.021	
50% Relative Humidity				
3		-0.011	-0.011	
4	-0.014	-0.019		
5	-0.014	-0.021		
6	-0.025	-0.025	-0.018	
7	-0.028	-0.029	-0.020	
10		-0.037		
14	-0.047	-0.034	-0.024	
21	-0.050	-0.039	-0.030	
49			-0.029	

**Table 3
Compressive-Strength Data, Class H Cement Mixtures**

Age (days)	23 °C	30 °C	38 °C	50 °C
100% Relative Humidity				
3	2890	3620	6020	5380
7	4310	6260	7810	5630
14	5920	6900	9230	5860
21		7730		
28	7320		8810	6170
37	8000		10500	6250
75% Relative Humidity				
3	3250	4930	5440	
7	3990	6220	7120	
14	4740	6150	7260	
21	5040	6080		
28	5320		7810	
37			7480	
50% Relative Humidity				
3	3190	3670	3800	
7	3480	4480	4330	
14	4040	4400	4800	
21	4140	4560		
28	4510		4830	
37			4380	

Table 4
Compressive-Strength Data, Type K Cement Mixtures

Age (days)	23 °C	30 °C	38 °C	50 °C
100% Relative Humidity				
3	4740	4930	6310	6980
7	6000	5910	8260	6780
14	6770	6470	8240	6910
21	8760	7000		
28	9760		8740	7760
37			9450	7380
75% Relative Humidity				
3	4300	5390	5950	
7	4950	6140	7370	
14	5360	6490	8290	
21	6280	7110		
28	6070		9290	
37			8440	
50% Relative Humidity				
3	4730	5910	6430	
7	5360 (8 d)	6760	6890	
14	5440	7000 (15 d)	7220	
21		6930		
28	6240		6980	
37			6960	

3 Results

Results

Data for length change and strength are summarized in Tables 1 through 4. Time-dependent length-change patterns are illustrated in Figures 1 through 6. Time-dependent strength-change patterns are illustrated in Figures 7 through 12.

Length change was always negative under conditions of 50 percent and 75 percent RH (Figures 1, 2 and 4, 5), regardless of temperature. The only positive length changes occurred at 100 percent RH. The positive change at 23 °C, 100 percent RH was unambiguous, but at higher temperatures under the same RH conditions, positive length changes occurred but were transient over days 3 through 5, and then became negative at later ages (see Figures 3 and 6). These negative values did not appear to be a result of drying due to accidental loss of RH in the storage cabinets because values were stable with time. The data may show even a slight tendency towards reversing the apparent shrinkage at later ages. One difference between the 100 percent RH condition at 23 °C and the 75 percent and 50 percent RH conditions was the presence of liquid water in the 100 percent RH condition. Specimens stored over water in sealed containers may have liquid water condense on their surfaces. If the storage temperature cycles, this will be more likely.

At the 23 °C and 100 percent relative humidity, ultimate expansion was greater in the Class H-based mixture (0.065 percent) than in the Type K-based mixture (0.020 percent). Length change stabilized by 14 days under these conditions in both mixtures.

Strength development responded to temperature and relative humidity about as expected from behavior of non-expansive systems, i.e. low relative humidity retards strength gain, while mildly elevated temperatures accelerate strength gain. The Type-K mixtures were generally stronger than the Class-H mixtures at equivalent ages. Low relative humidity caused strength development to cease, and, in the case of 38 °C storage, strength tended to be lower at the last test age (37 days) than at earlier ages. These apparent changes in strength are small relative to the variation among cubes at each test age, suggesting that they are a coincidental consequence of testing precision. Strength gain at 50 °C was severely retarded relative to gain at the other test temperatures.

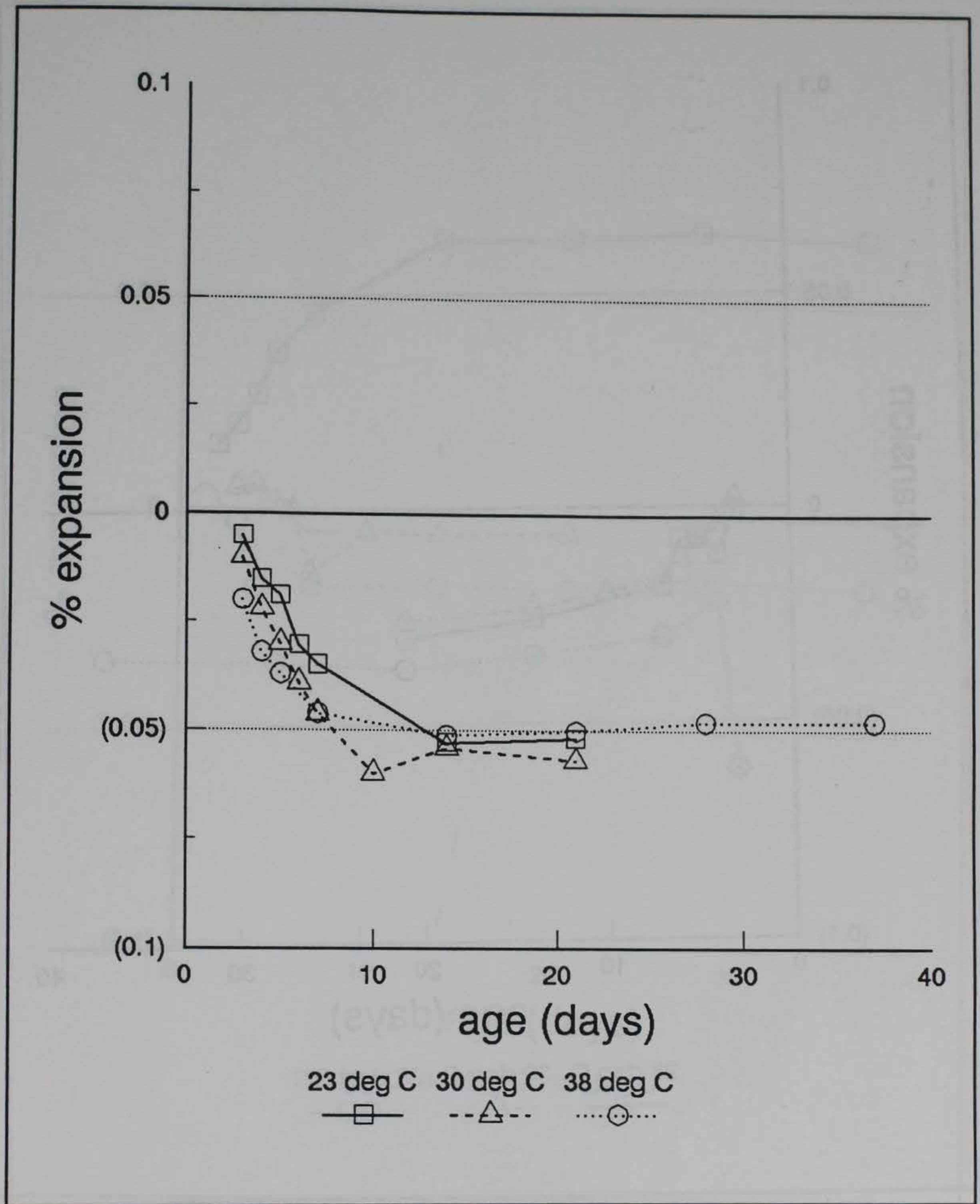


Figure 1. Expansion versus age 50 percent relative humidity Class H cement

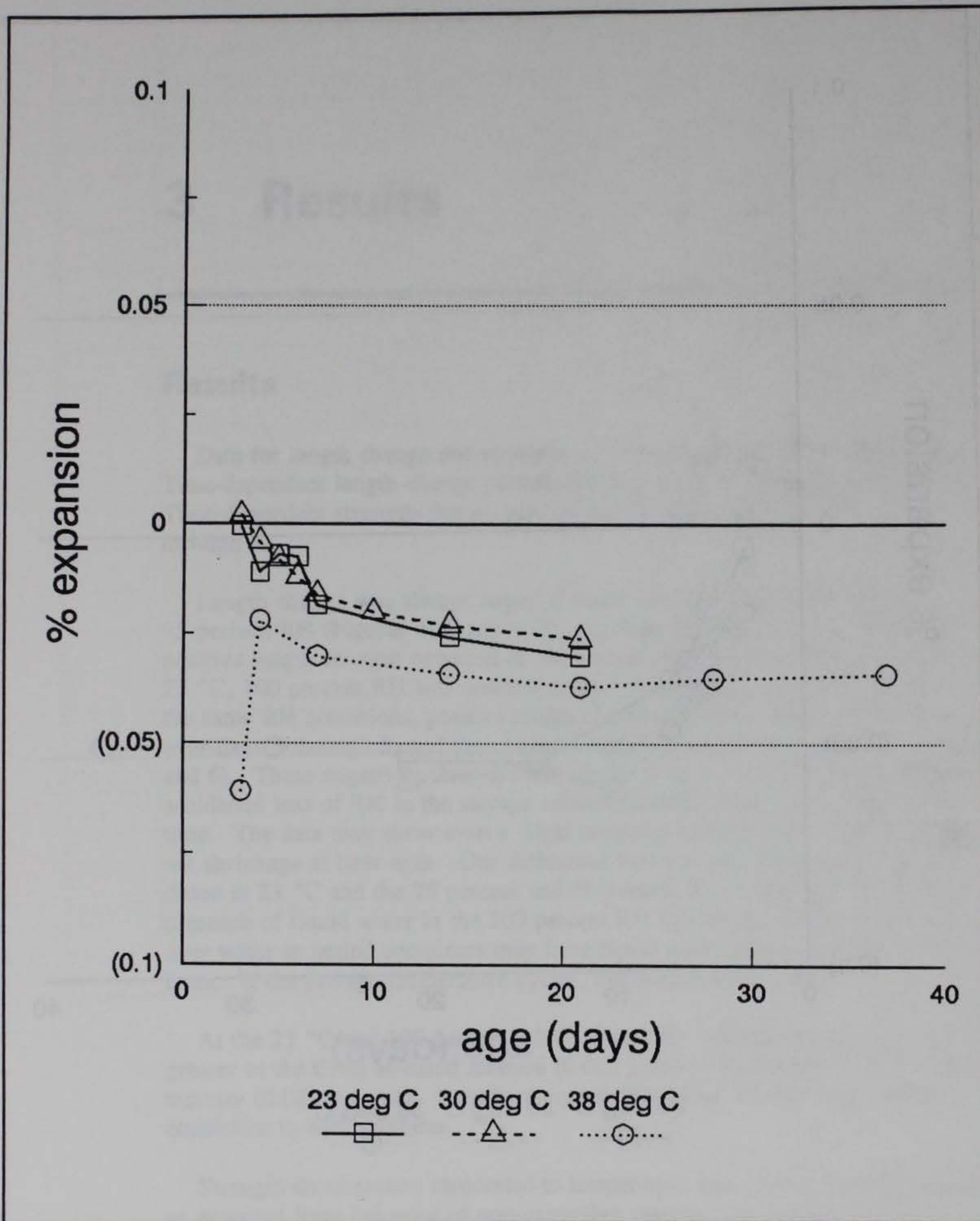


Figure 2. Expansion versus age 75 percent relative humidity Class H cement

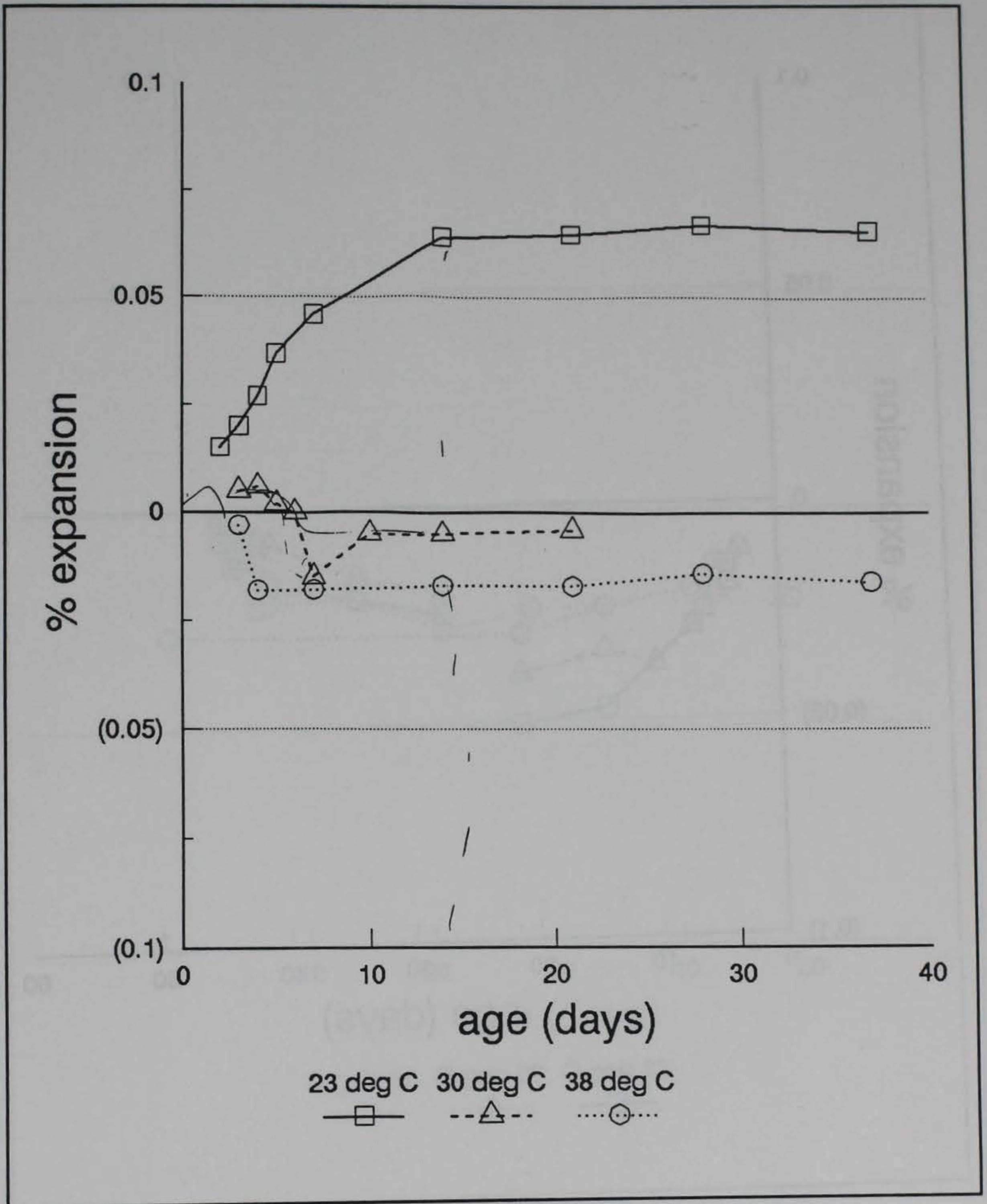


Figure 3. Expansion versus age 100 percent relative humidity Class H cement

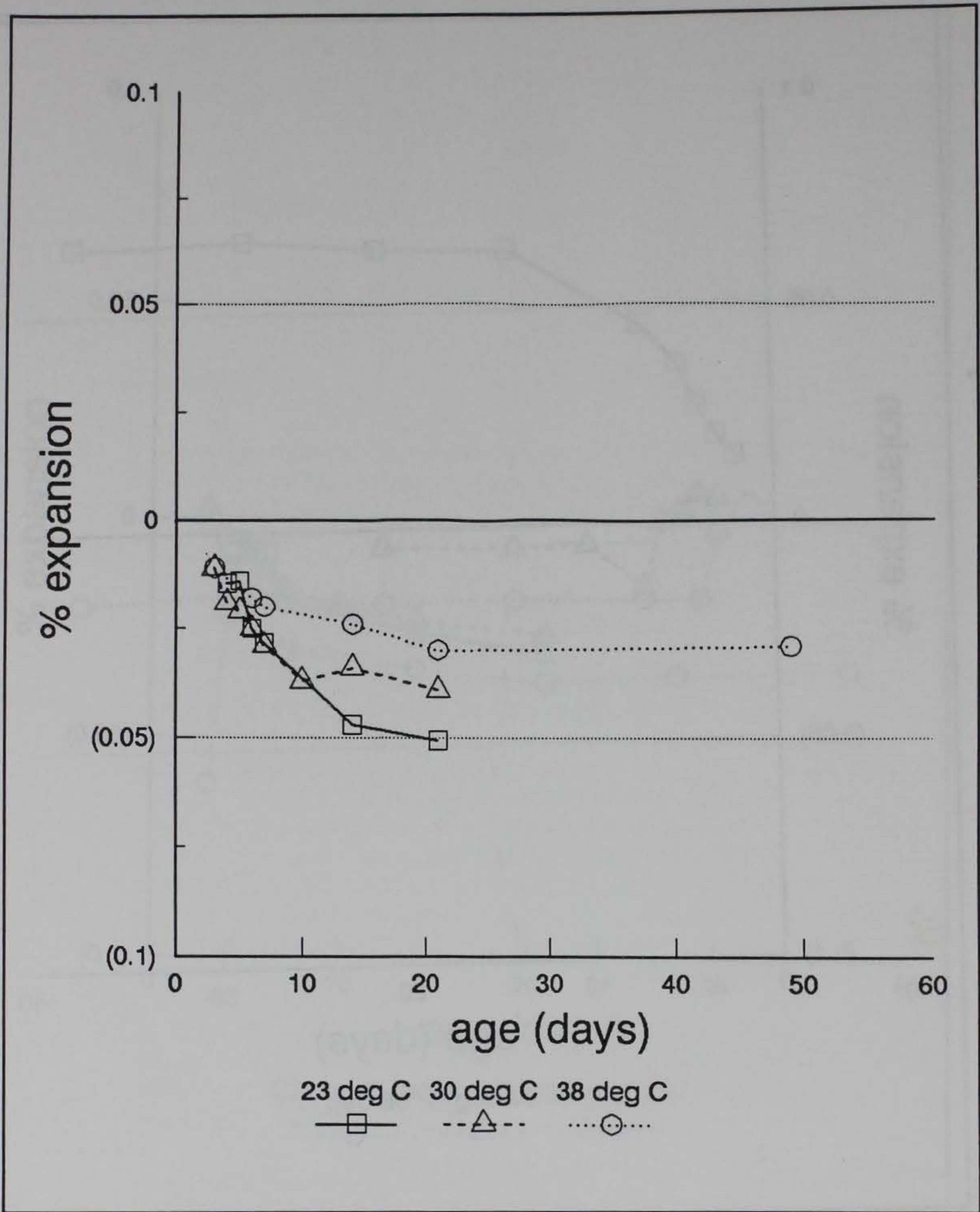


Figure 4. Expansion versus age 50 percent relative humidity Type K cement

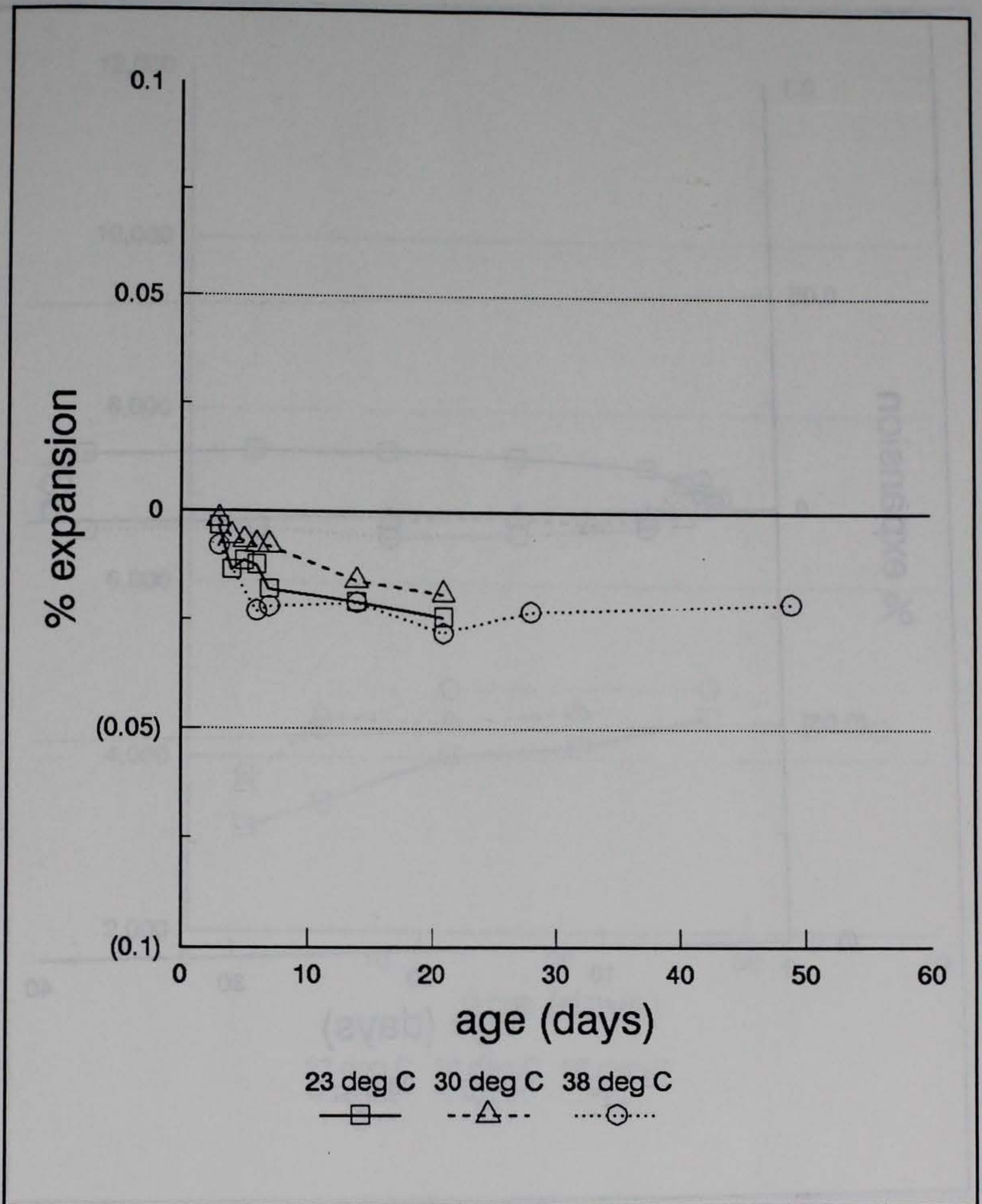


Figure 5. Expansion versus age 75 percent relative humidity Type K cement

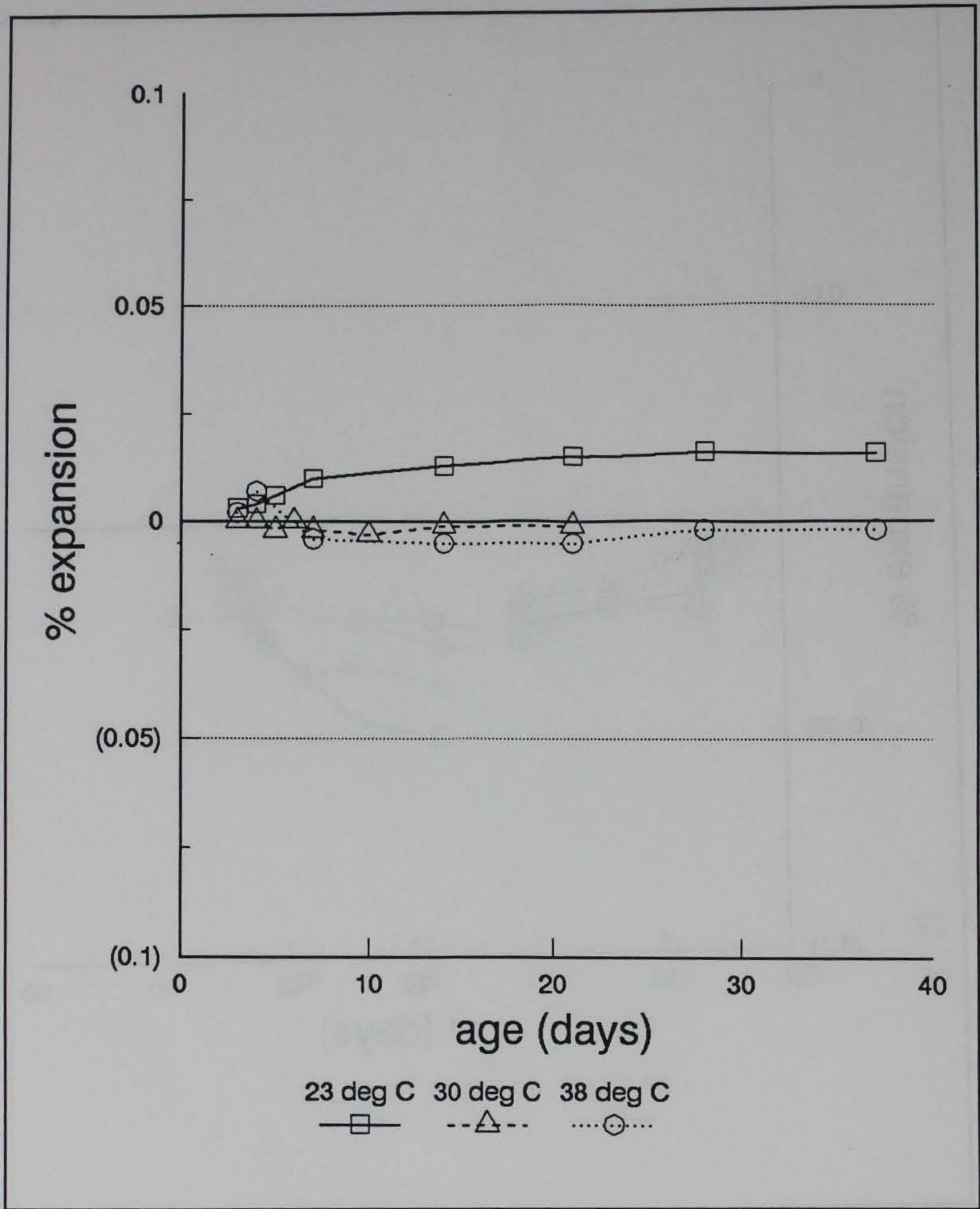


Figure 6. Expansion versus age 100 percent relative humidity Type K cement

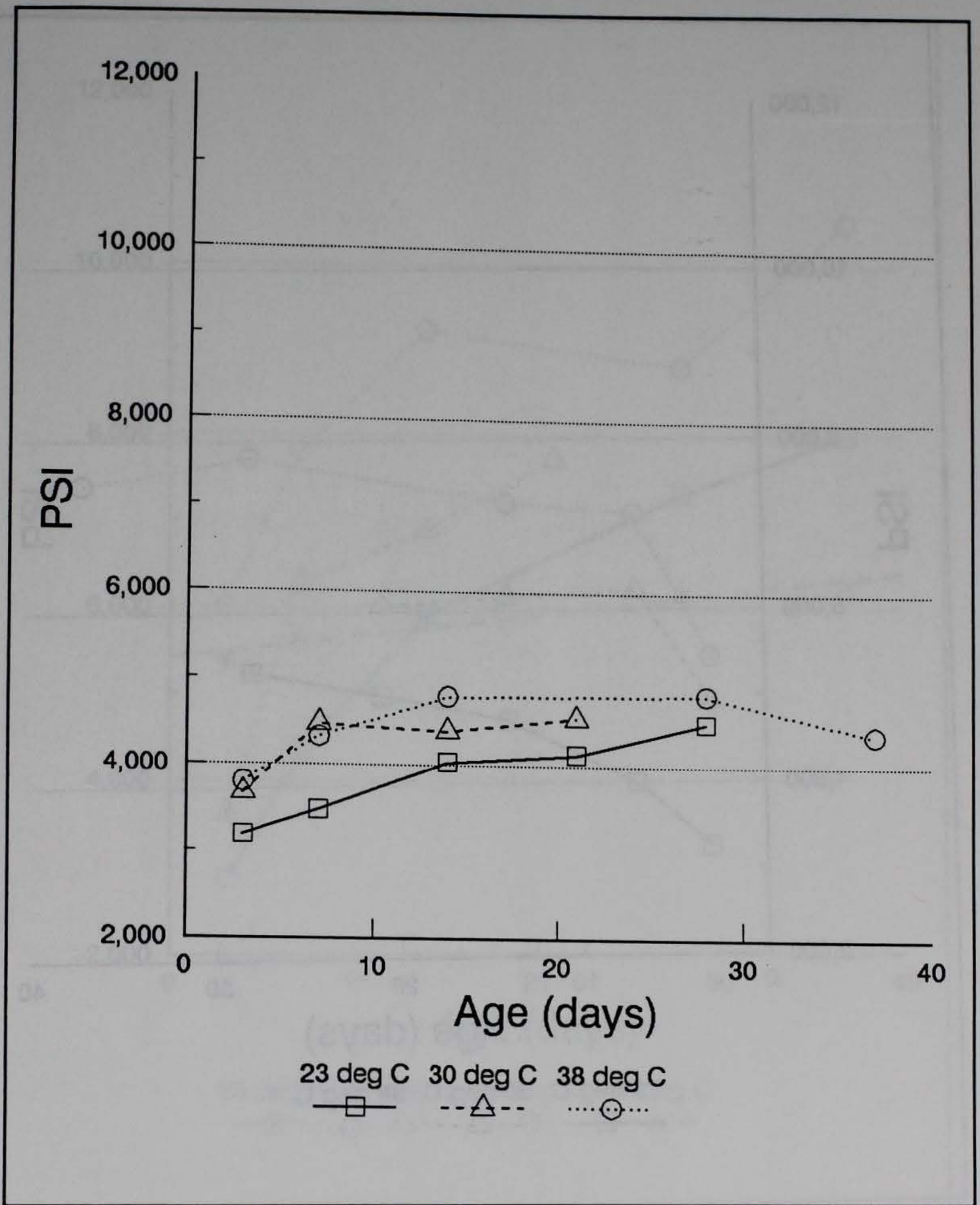


Figure 7. Strength versus age 50 percent relative humidity Class H mixtures

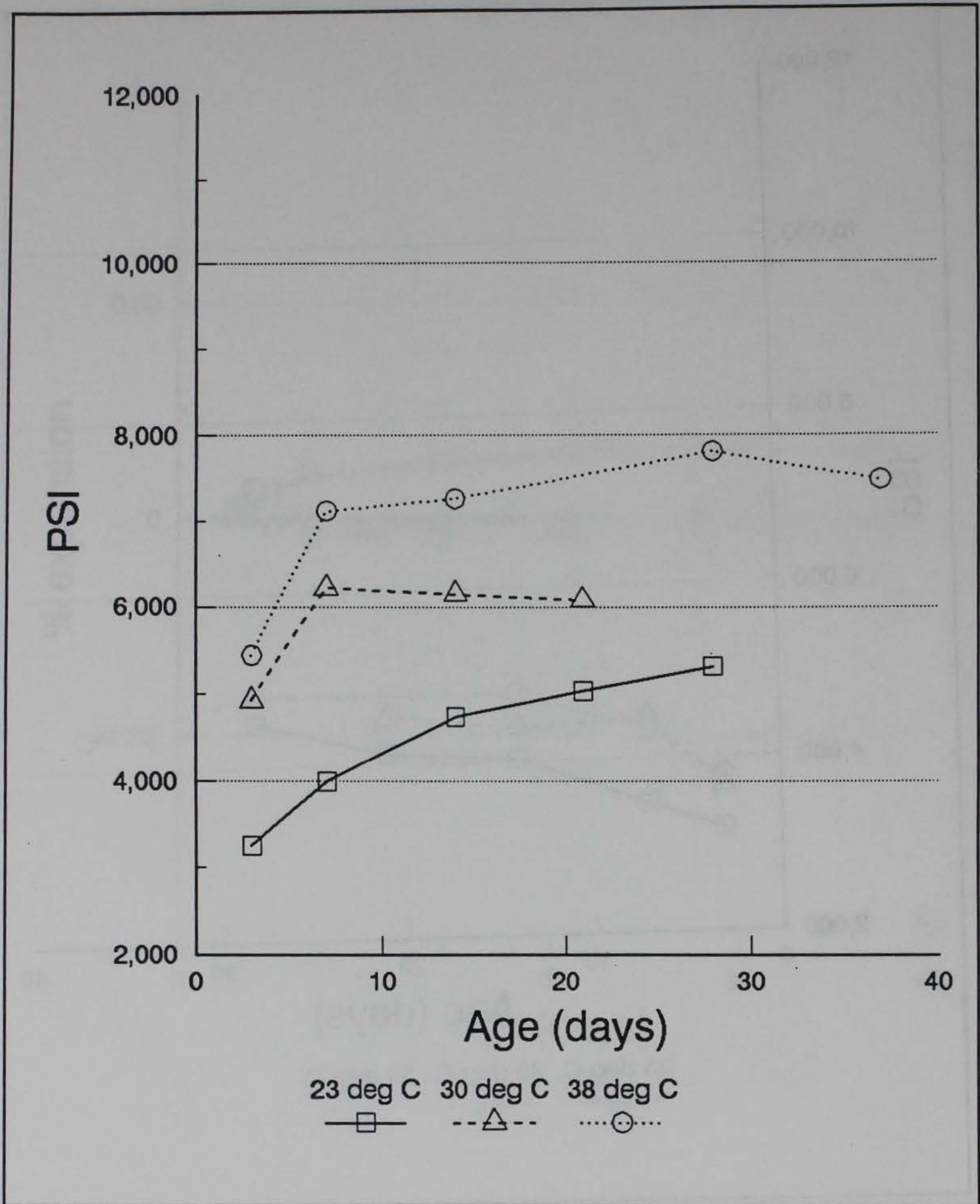


Figure 8. Strength versus age 75 percent relative humidity Class H mixtures

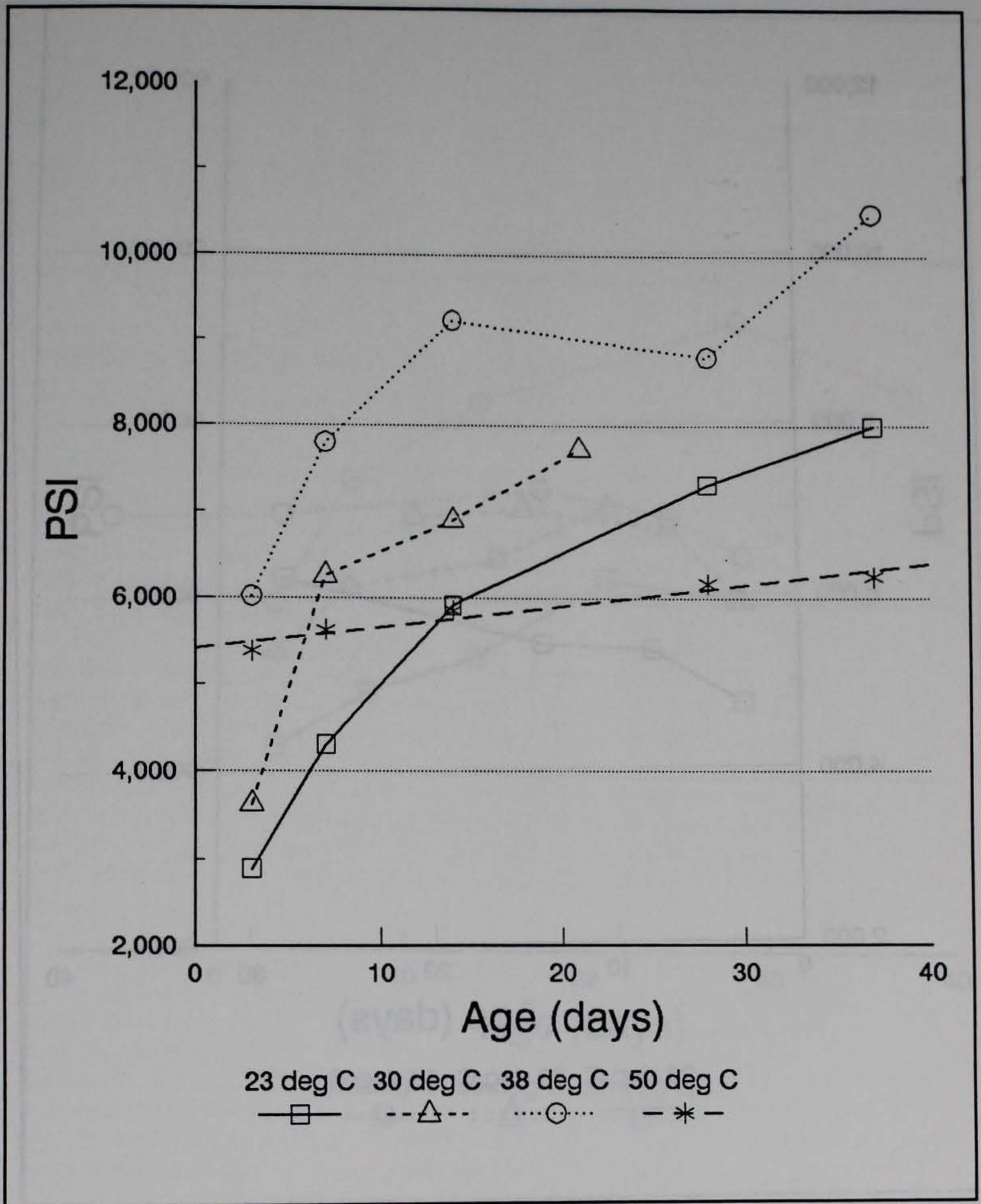


Figure 9. Strength versus age 100 percent relative humidity Class H mixtures

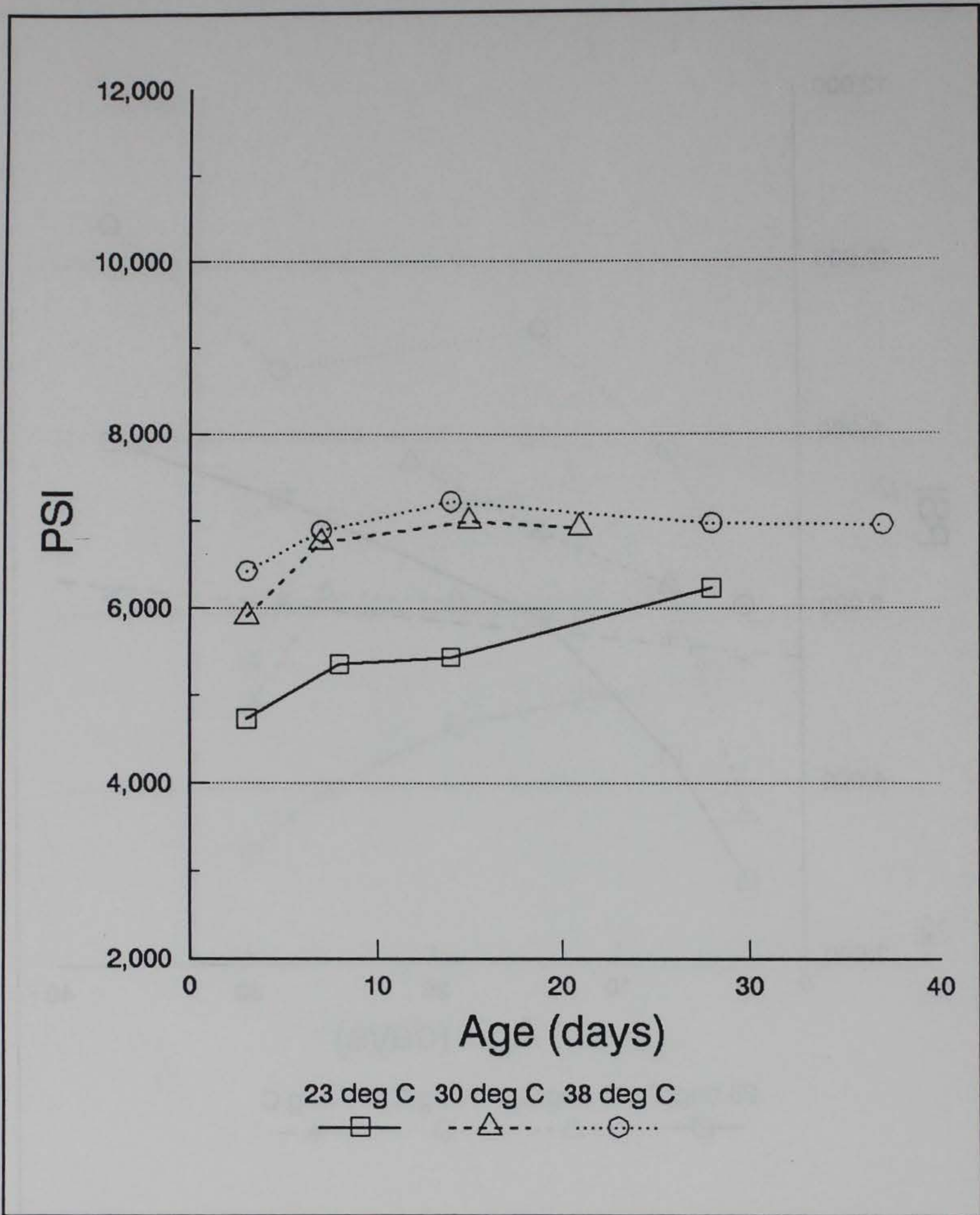


Figure 10. Strength versus age 50 percent relative humidity Type K mixtures

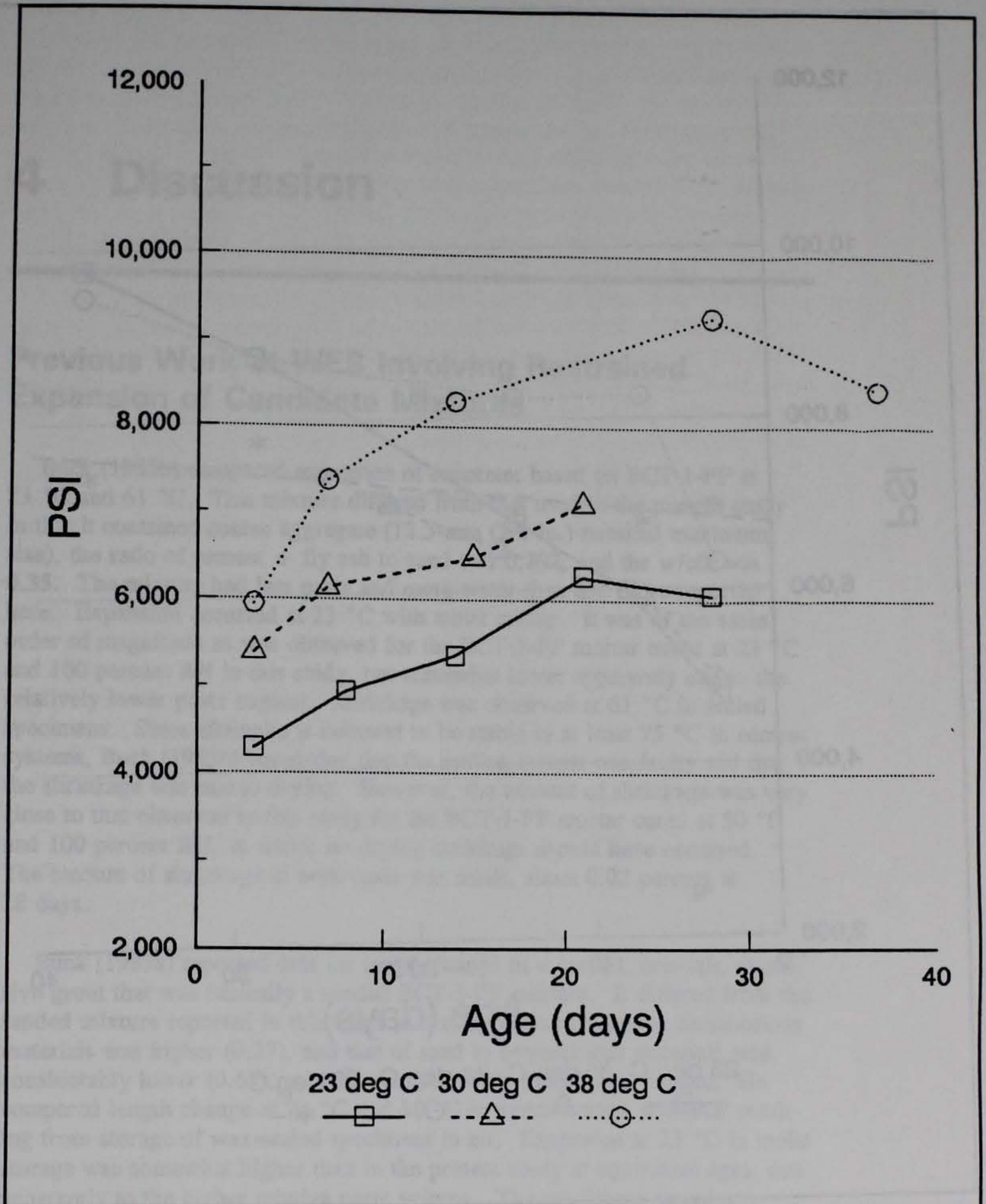


Figure 11. Strength versus age 75 percent relative humidity Type K mixtures

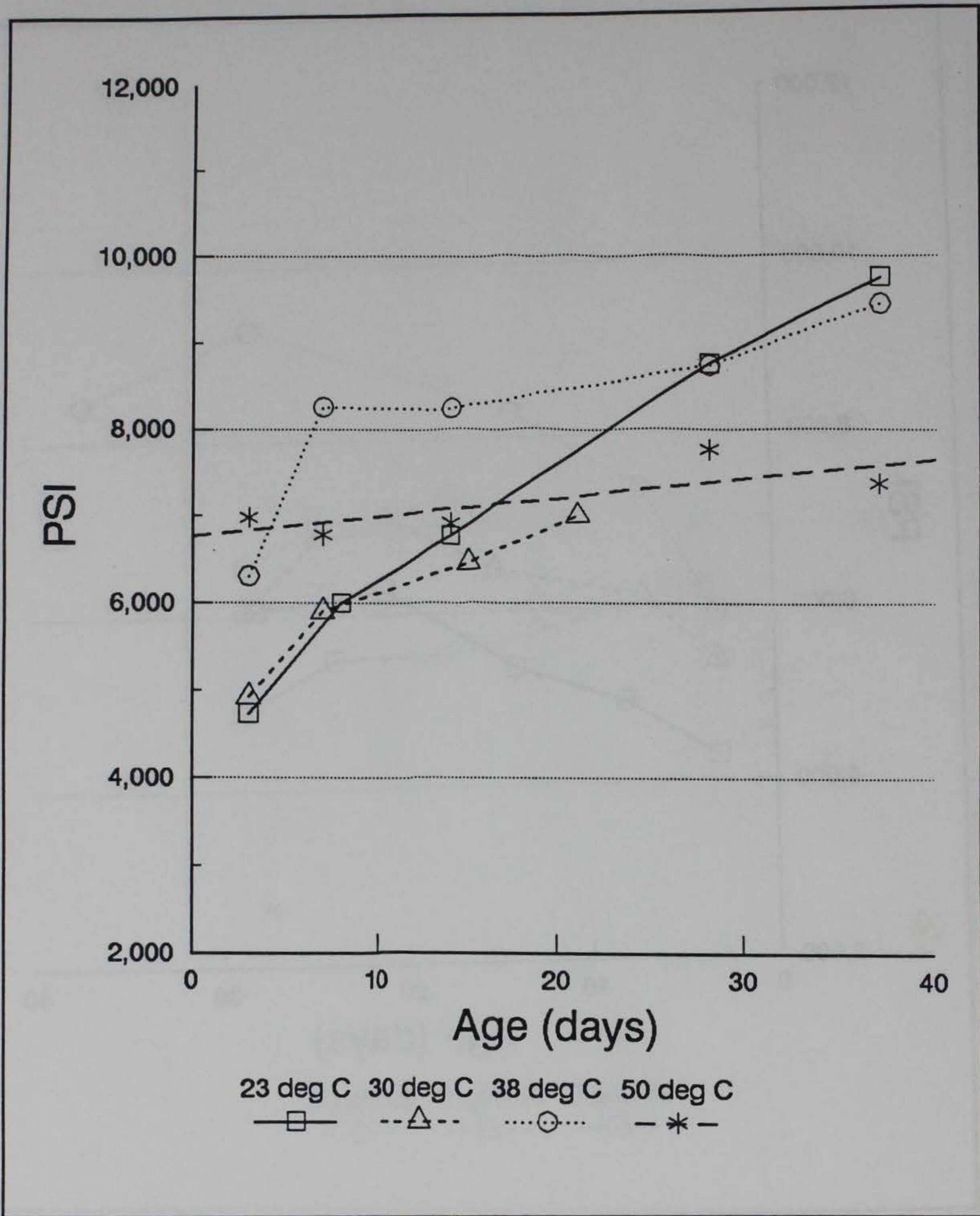


Figure 12. Strength versus age 100 percent relative humidity Type K mixtures

4 Discussion

Previous Work at WES Involving Restrained Expansion of Candidate Mixtures

Buck (1985b) compared expansion of concretes based on BCT-1-FF at 23 °C and 61 °C. This mixture differed from that used in the present study in that it contained coarse aggregate (12.5-mm (1/2-in.) nominal maximum size), the ratio of cement + fly ash to sand was 0.292, and the w/cfa was 0.35. The mixture had less paste and more water than had those reported here. Expansion occurred at 23 °C with moist curing. It was of the same order of magnitude as was observed for the BCT-1-FF mortar cured at 23 °C and 100 percent RH in this study, but somewhat lower apparently due to the relatively lower paste content. Shrinkage was observed at 61 °C in sealed specimens. Since ettringite is believed to be stable to at least 75 °C in cement systems, Buck (1985b) concluded that the sealing system was faulty and that the shrinkage was due to drying. However, the amount of shrinkage was very close to that observed in this study for the BCT-1-FF mortar cured at 50 °C and 100 percent RH, in which no drying shrinkage should have occurred. The amount of shrinkage in both cases was small, about 0.02 percent at 28 days.

Buck (1985a) reported data for length change of a sanded, non-salt, expansive grout that was basically a sanded BCT-1-FF mixture. It differed from the sanded mixture reported in this work in that the ratio of water to cementitious materials was higher (0.37), and that of sand to cementitious materials was considerably lower (0.67), so there was relatively more paste volume. He compared length change at 23 °C and 30 °C in moist storage with that resulting from storage of wax-sealed specimens in air. Expansion at 23 °C in moist storage was somewhat higher than in the present study at equivalent ages, due apparently to the higher relative paste volume. The specimens stored at 30 °C also expanded, then lost some expansion (relative negative length change), then expanded again at about 56 days. Specimens stored at 30 °C, but wax sealed and in air, expanded early but then lost the expansion at later ages (one eventually showed negative length changes, the other showed a relative reduction in expansion, but never reached zero). Buck attributed the loss of the early expansion in the waxed bars to drying, but recommended further study to verify this.

Data for expansion of unsanded grouts representing several combinations of materials were reported by Buck et al. (1983). Specimens were stored in saturated lime water at 23 °C. Expansion of the BCT-1-FF mixture was very slow to develop, showing negative values at 7 days, but expansions at 28 days were comparable to those reported in the present study. Changing the source of the fly ash resulted in a several fold increase in expansion, probably attributable to differences in chemical composition, or particle size, or both.

Effects of curing temperature and water availability (inundation versus wrapped and bagged) was reported by Gulick, Boa, and Buck (1980). In comparisons of paste specimens cured at 53 °C, inundated specimens expanded 0.05 percent at 56 days (somewhat less expansion than observed at 23 °C in the present study), while wrapped and bagged specimens showed negative length change of -0.03 percent. It was concluded that drying shrinkage through a faulty sealing system was responsible for the latter. There was also a temperature effect among inundated specimens. Specimens stored at 23 °C expanded more at 28 days (0.020 percent) than specimens stored at 53 °C (0.010 percent); but by 100 days, expansion in both groups was about the same (0.055 percent).

Probable Causes of Observed Expansion

It was expected that expansion at elevated temperatures and 100 percent RH would occur. The failure of such behavior to occur had been attributed to imperfect control of curing conditions. In most of these cases, the conditions for 100 percent RH were established by wrapping the bars in a plastic membrane and then double bagging with plastic bags with storage in laboratory air. There were generally no data reported in support of the drying-shrinkage hypothesis. Rather, it was taken as a plausible explanation for the apparently deviant behavior. This hypothesis is plausible for long-term storage conditions, because plastic does allow some transmission of moisture. However, this type of triple-layer sealing system should provide conditions close to 100 percent RH for a period of a month or so, such as those of the present study. Most of the suspect data from previous work reported no expansion even at very early ages. The results obtained in the current work, in which no drying was allowed because of the 100 percent RH condition, suggest that some other mechanism may be contributing to this phenomenon.

A review of the literature on the mechanisms of expansion in systems that rely on formation of ettringite may be enlightening. The exact mechanism by which expansion accompanies formation of ettringite is not universally agreed upon. Expansion appears to accompany formation of ettringite, but formation of ettringite does not always result in expansion. There are said to be at least two schools of thought on the mechanism by which formation of ettringite causes expansion. These were reviewed by Cohen (1983a). These are not necessarily mutually exclusive, nor are they necessarily inclusive of all possibilities, as was discussed by Mather (1984).

One hypothesis is that expansion occurs when very small ettringite crystals form. These have a high surface area, resembling a gel. Under this hypothesis, it is believed that the formation of the ettringite per se does not cause expansion, because the total volume of the reaction products is less than the total volume of the reactants. But, it is hypothesized that, this gel swells by imbibing water. This hypothesis would require that water be taken into the system. According to this mechanism, no swelling occurs if ettringite crystals are large or if water is not available. This hypothesis is often called the swelling hypothesis.

According to the other hypothesis, expansion occurs because of the growth of ettringite crystals on the surface of calcium aluminates. Solid sulfates are hypothesized to dissolve and sulfate ions are said to diffuse towards the aluminate sites; this is a through-solution reaction. The total volume of the reaction products is slightly smaller than the total volume of the reactants (including water), so linear growth of a crystal in a rigid matrix is hypothesized to cause expansion not by increasing the total volume of solid in the system but rather by leaving empty space formally occupied by water. This hypothesis is often called the crystal growth hypothesis.

It is most likely that when there is expansion of concrete, mortar, or grout resulting from a chemical reaction between sulfate ion in solution and chemically active aluminates in portland cement or expansive cement, the expansion is caused by topochemical, in situ, sulfation of the aluminate (Mather 1984). This concept assumes that crystal growth from solution never results in any force being exerted on the surroundings--a bottle containing a supersaturated solution is not broken by letting evaporation remove solvent so that crystals precipitate from the solution.

Odler and Gasser (1988) performed a detailed investigation into the mechanism of sulfate-based expansion in a portland-cement system. They found that the amount of expansion depended to some degree on externally derived water. There was enough water in the mixture to give some expansion in their sealed samples, but storage in water-saturated air resulted in more expansion, and storage in immersed conditions resulted in even more expansion. Their interpretation of these results was that at least some of the expansion must be due to crystal growth, since no water uptake was required for some expansion to occur. However, the enhanced expansion when water was taken up was viewed as evidence for a swelling component to the total expansion. Independent evidence for the latter was obtained by fabrication of pastes made from ettringite and tricalcium silicate (C_3S , a component of portland cement) which expanded when immersed, but did not when cured in saturated air.

Negro and Bachiorrini (1982) examined the effect of temperature on ettringite-based expansion. Their temperature range was 22 °C to 60 °C. Early expansion generally increased with temperature, but this trend was less apparent at the higher temperatures. Also, the higher temperature conditions resulted in all expansion being depleted by about 3 days, while expansion in lower temperature conditions continued to about 7 days. SEM work indicated that the differences in the size of the ettringite crystals under different

experimental conditions correlated with the observed expansion phenomena. They interpreted their results in the context of the swelling hypothesis. Although the temperatures are different, it suggests that temperature could accelerate the expansive reaction to the point that it is largely dissipated by the age of the first length-change calculation. In extreme cases, a reaction that normally causes expansion may fail to do so if it approaches equilibrium before a rigid hydrated cement matrix is established. That is, if the ettringite-forming reaction is accelerated more than the strength-gain process, much of the desired expansion due to ettringite formation will be lost, since it takes place before the concrete is strong enough to expand due to internal volume change. This leaves the empty space previously occupied by the sulfate solution.

Panchenko (1990) investigated the effect on expansion of mortars by adding calcium hydroxide. Addition of lime resulted in increased expansion. The purpose of his work was to find a way to engineer levels of expansion, and Panchenko concluded that control of the addition of lime could do this. However, his results may have some importance in understanding expansion in systems containing fly ash. Because lime is consumed by reaction with a pozzolan such as fly ash, plausibly the amount of uncombined lime in blends of fly ash and portland cement varies with the relative amount of the pozzolan and the degree of hydration. This may explain some of the differences observed in expansion among mixtures containing different fly ashes. However, in a system with 65 percent portland cement and 35 percent fly ash there should be sufficient, available calcium to keep the pore fluid saturated and to produce CSH from all the silica in the cement and the fly ash and maintain a saturated Ca(OH)_2 solution in the pore fluid permanently.

In a discussion of the effects of water-cement ratio (w/c) on cement hydration, Philleo (1983) expressed concern over the effects of self-desiccation in low w/c systems. His principal concern was over the differences in strength that would be developed when low w/c specimens are cured in water, compared with the strength that would develop when additional water is not available. Perhaps a similar concern should apply to developing expansive systems. This problem has been encountered in tunnel grouting. It was at least partly overcome by the use of saturated lightweight coarse aggregates as a source of additional water.

Bensted (1983) examined the relationship between w/c and ettringite formation at very early ages (2 hours). In his studies, about 30 percent more ettringite was formed at w/c of 0.5 than at w/c of 0.3. The work was not directed to expansive systems, but the results may be applicable in the context of Philleo's considerations.

5 Conclusions and Recommendations

Water availability and temperature are perhaps more critical variables than was believed when mixtures were first designed for the WIPP. Given that in-place concrete may not have access to externally derived water, and may be warmed by heat of hydration in mass placements, expansion may not be simply predicted. Mixtures with the chemical potential to be slightly expansive may actually shrink. All mixtures should be evaluated for expansive properties under moisture and temperature conditions that will apply in the placement.

Cohen (1983b) has emphasized the need to model expansion, to ensure that the needed amount of expansion is in fact obtained in situ and, further, to ensure that excessive expansive forces are not generated that could cause disruption of non-restrained placements. Placement conditions therefore should be considered for each use of concrete in the WIPP. Some placements will be entirely restrained, while others will be open on at least one side. Open surfaces, or surfaces in contact with a temporary bulkhead (formwork) instead of rock, will create microclimates of moisture and temperature conditions. From work on the first expansive salt-saturated concrete developed by WES for the WIPP, we know (Wakeley and Walley 1986) that slight changes in these conditions can affect measurable properties of a strongly expansive concrete. The present work indicates that the factors of temperature and humidity are more critical to the performance of less exotic mixtures as well. It demonstrates the control on early-age properties of cement-based materials that can be exerted by variables of the service environment.

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As part of materials development studies for the Waste Isolation Pilot Plant (WIPP) Plugging and Sealing Program, we studied two freshwater sanded grouts proportioned with materials having potential for expansion. Length change (expansion or shrinkage) and strength development were measured following curing and storage at temperatures from 23 to 50 °C and relative humidities from 50 to 100 percent.

Length change was negative at all temperatures at RH values of 75 percent and less. Decidedly positive length change (expansion) occurred only when samples were stored at 100 percent RH, and even this reversed with time at the higher temperatures. Low relative humidity also inhibited strength gain, as did storage at 50 °C, but temperatures up to 38 °C favored higher strength.

This work demonstrates the control on both early-age and long-term properties of cement-based materials that can be exerted by variables of the service environment.

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