

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

### Dewatering Fine Coal Slurries by Gel Extraction

Stevin H. Gehrke; Lii-Hurng Lyu; Kristopher Barnthouse

**To cite this Article** Gehrke, Stevin H. , Lyu, Lii-Hurng and Barnthouse, Kristopher(1998) 'Dewatering Fine Coal Slurries by Gel Extraction', Separation Science and Technology, 33: 10, 1467 — 1485

**To link to this Article:** DOI: 10.1080/01496399808545061

**URL:** <http://dx.doi.org/10.1080/01496399808545061>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Dewatering Fine Coal Slurries by Gel Extraction

---

STEVIN H. GEHRKE,\* LII-HURNG LYU,  
and KRISTOPHER BARNTHOUSE

DEPARTMENT OF CHEMICAL ENGINEERING  
UNIVERSITY OF CINCINNATI  
CINCINNATI, OHIO 45221-0171, USA

### ABSTRACT

Gel extraction is evaluated as a novel technique for dewatering fine coal slurries. This technique uses temperature-responsive gels to absorb water from slurries at low temperatures; after separation of the swollen gel from the dewatered slurry, the gel is heated slightly above ambient temperature, which causes it to release the water it absorbed. The gel can then be recycled. The equilibrium and kinetic properties of poly(*N*-isopropylacrylamide) gel were evaluated for utility in this process. The gels effectively dewatered slurries to around 70 wt% solids; performance was not a strong function of particle size, though coarser slurries ( $-16$  mesh) could be dewatered to greater extents than the finer slurries ( $325 \times 400$  mesh). The gels showed no sign of deterioration over a period of 2 months and 20 cycles.

### INTRODUCTION

Coal utilization is closely linked to the ability to remove undesirable constituents. Physical coal cleaning is not simply the employment of a single process, but rather involves the combination of several operations. Usually six major operations—crushing, sizing, cleaning, slurry dewatering, clarifying, and coal drying—are used. Cleaned coal is separated into three size fractions: coarse, intermediate, and fine. In general, the more finely crushed the coal, the higher the quality of the resulting cleaned coal. The finer the coal, however, the more difficult it is to dewater the resulting slurries. It is

\* To whom correspondence should be addressed.

therefore desirable to reduce the capital and operating costs of the equipment used for dewatering fine coal slurries.

A new separation method, gel extraction, is a possible alternative dewatering method. Originally gel extraction was developed to separate water and low molecular weight solutes from a variety of macromolecular solutes, such as proteins, based on size exclusion of the large solutes from the gel network (1–5). In these processes, the use of stimuli-responsive polymer gels (i.e., gels whose volume can be varied by small changes in environmental conditions, such as temperature, pH, ionic strength) means that the gels are easily reused, since the water they absorb can be released by modest changes in temperature, pH, etc. Since slurries contain much larger particles than macromolecular solutions, based on the principle of size exclusion, gel extraction should dewater slurries of different properties well. Some research on the use of gels for dewatering slurries and sludges of biological origin has been carried out (6, 7). A related process has also been patented for using gels to dewater drilling muds (8). However, many questions remain, including the extent of dewatering possible and factors that affect the economics like service lifetime of the gels.

The gels at the heart of this study can swell 2–50 times their dry weights by absorbing water at a low temperature while excluding particulates from their crosslinked structure. The operating principles of temperature-driven gel extraction are illustrated in Fig. 1. The gel in its shrunken form is immersed

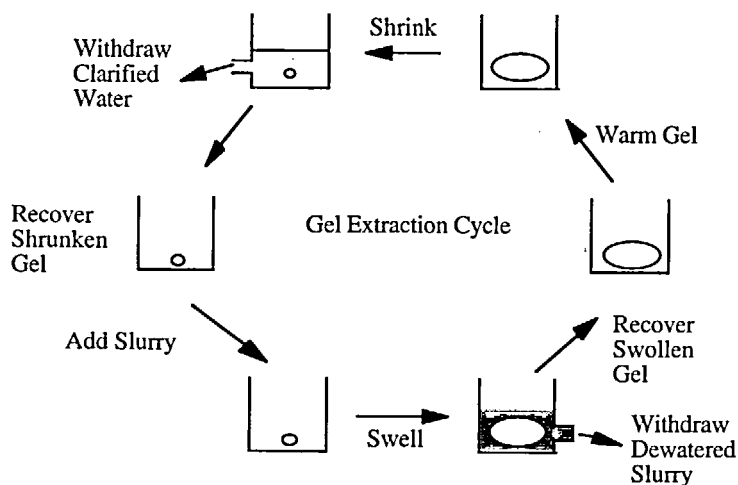


FIG. 1 The gel extraction cycle using temperature-sensitive gels for slurry dewatering. The key advantage is that the process is driven by slight warming of the reusable gel above ambient temperatures.

in the coal slurry. If the slurry is at ambient temperature or cooler, the temperature-sensitive gel swells, absorbing water from the slurry while excluding all particulates which are too large to penetrate the polymer network. Next, the swollen gel is removed from the dewatered solution. After warming above ambient temperature, the gel reverts to its shrunken form, expelling the water it absorbed from the slurry; this water is virtually free from particulates. The gel can now be reused in further concentrating cycles (4, 5, 8).

The specific objectives of this research were to synthesize and characterize a temperature-sensitive gel, to examine the rates and variables affecting water sorption/desorption by the gel, to determine the effectiveness of gel extraction in removing water from coal slurries, to determine the service lifetime of gels, and to consider the practical aspects of gel extraction when used for slurry dewatering.

## EXPERIMENTAL METHODS

### Gel Synthesis

The poly(*N*-isopropylacrylamide) (PNIPA) gels used for this study were prepared through free radical solution copolymerization/crosslinking reaction. The crosslinker was *N,N'*-methylene-bisacrylamide. Gels of different monomer and crosslinker weight fractions were prepared in order to find a gel of suitable characteristics for gel extraction. Composition was indicated using the notation " $X \times Y$ ," where  $X$  is the mass percent of monomer and crosslinker in the reaction solutions, while  $Y$  is the crosslinker mass percent relative to the total monomer plus crosslinker. Gels in this study were prepared as flat sheets, 0.1 or 0.2 cm thick, in an oxygen-free glove box by pouring the reaction mixture (including initiators) between glass plates separated by gaskets of appropriate thicknesses. Polymerization was allowed to occur for 24 hours at 5°C. Details of the gel synthesis are published elsewhere (9).

In order to characterize the equilibrium swelling degree for each gel at various temperatures, a gravimetric technique was employed (10, 11). The crosslink density of each gel formulation was determined from stress vs strain measurements of the gels under uniaxial compression using the equipment and methods described by Harsh and Gehrke (12, 13).

### Kinetics Experiments

Work was done to establish the rates of heat transfer and water sorption/desorption in a gel extraction cycle. A  $k$ -type thermocouple was inserted along the centerline of a cylindrical gel. The gel was allowed to equilibrate in a water bath at ambient temperature. The gel was quickly removed and placed into a second water bath at some final temperature. The

gel centerline temperature was recorded as a function of time until it reached the final temperature. In a separate experiment, gels of the same composition were subjected to similar temperature changes. The gravimetric method was used to identify the mass change in each gel at given centerline temperatures. In this way, rates of heat and mass transfer for a gel could be compared. The dimensional dependence of sorption/desorption kinetics was also studied to determine if, in fact, a diffusion coefficient based upon an analysis of Fick's law could quantify the sorption/desorption rates as described by Kabra et al. (10, 11, 14). Finally, the kinetics were studied as a function of temperature and gel composition. One set of experiments examined the rates of swelling or shrinking away from a common equilibrium; specifically, gels equilibrated at 25°C were caused to swell at 5, 10, 15, and 20°C, and to shrink at 30, 32, 35, and 37°C. The gels were then returned to 25°C, shrinking for warmed samples and swelling for cooled samples.

### Slurry Dewatering Experiments

The slurry dewatering experiments served to establish the effectiveness of gel extraction by examining the extents of dewatering possible for different coal slurries and the dewatering rates. The coal used was a blend of #8 and #9 coals from the Lamira Preparation Plant (Lamira, OH) of the R&F Coal Company. The coal samples were dry ground and separated with sieves into several size fractions. These fractions were used to form slurries ranging from 10 to 90 wt% solids by mixing with distilled water [Distilled water was used as a convenient reference solvent. Since the swelling characteristics of nonionic gels such as PNIPA are not significantly influenced by ions, the results obtained should be the same for any coal slurry prepared using any fresh water source (13). However, if a slurry solution is significantly brackish (ionic strength  $> 0.1$  M), the swelling degrees and transition temperatures may be altered, though without a qualitative change in gel performance (15)].

It was noted that coal particles tend to stick to the surface of gels, but do not have any measurable effect upon the gel performance. For this reason, each gel sample was precoated with coal slurry, preventing a fresh gel from picking up coal particles from the experimental slurries simply by adsorption. The precoated gel was first allowed to equilibrate at 32°C for 2 days and then rinsed of loose particles prior to experiments (the results of the kinetics experiments showed that this was sufficient to reach equilibrium). After experiments, the gel was reshunk at 32°C to examine if loss of mass had occurred; if the mass balance could not be closed, the experiment was discarded.

To determine the effect of slurry solids content on dewatering effectiveness, in one set of experiments the gel slabs were immersed into a large excess of coal slurry at 25°C. In another set of experiments the different gel/slurry ratios

were used to determine the extent of dewatering possible for each coal size fraction, starting from a 40 wt% solids slurry, with dewatering occurring at 25°C.

### Service Lifetime Experiments

To determine the cycling lifetime of the gel, samples of  $10 \times 4$  and  $16 \times 1$  gels were immersed into coal slurry or water and equilibrated for 1 to 2 days at 5 °C. After being blotted and weighed, the gels were transferred to identical slurries or water at 32°C and were again allowed to equilibrate. This process was repeated for a total of 20 times over a 2-month period. After these cycles, swelling and shrinking tests were performed, and the results from these gels were compared to those of similar gels from the kinetics experiments.

To estimate if abrasive degradation is likely to be a problem, gel samples were immersed into slurries with both perpendicular and parallel orientations of the surface of the gel to the flowing slurry which was stirred at 150 or 400 rpm. The slurry of  $48 \times 100$  mesh coal at 40 wt% solids was used. After stirring continuously for 1 week, the gel was examined under a microscope to compare exposed and plastic-covered, protected gel areas.

## RESULTS AND DISCUSSION

### Gel Characterization

Of the synthesized gels, four characteristic compositions were selected for later experiments based upon their visible appearance (opaque or transparent), flexibility, texture, mechanical strength, and equilibrium swelling ratio. Gels of monomer content below 10% were easily broken and had a sticky texture, making them unacceptable for gel extraction. The four selected gels included  $10 \times 1$ ,  $10 \times 4$ ,  $16 \times 1$ , and  $16 \times 4$ , thus covering a broad range of monomer and crosslinker concentrations, while maintaining good flexibility and handling characteristics.

The temperature sensitivity of these gels is shown in Fig. 2 which shows their equilibrium swelling ratios ( $q$  = hydrated mass of the gel relative to the dry mass of the gel) as a function of temperature. A sharp decline in the water sorption capacity of the gel—about a factor of 10—is seen between 25 and 35°C, with half the collapse occurring abruptly at 33°C. Figure 2 shows that gel composition greatly influences swelling below the collapse temperature but not above it, where the water content of all gel formulations is low. It can also be noted that gels which exhibit high swelling ratios are gels low in monomer and crosslinker concentration, conditions which were measured to produce gels with smaller effective crosslink densities, thus re-

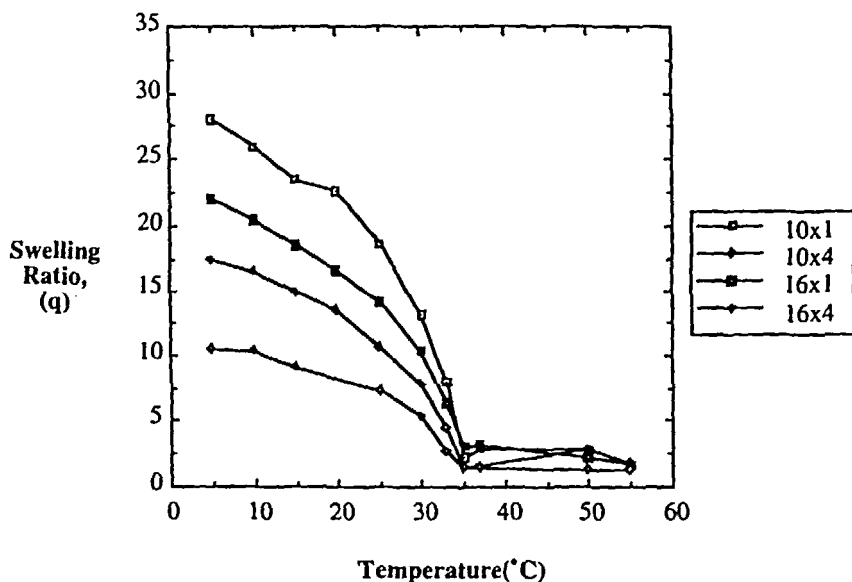


FIG. 2 The swelling of different formulations of poly(*N*-isopropylacrylamide) gel as a function of temperature. Composition is indicated using the notation "X × Y," where X is the mass percent of monomer and crosslinker in the reaction solutions, while Y is the crosslinker mass percent relative to the total monomer plus crosslinker.

sulting in gels with greater swelling (9). Clearly a higher swelling gel is desired for dewatering, but this has to be weighed against the kinetics and service lifetimes of the different gels in terms of overall performance.

### Kinetics of Gel Sorption/Desorption

#### Heat Transfer

Before the gel will undergo a volume change, its internal temperature must change. As demonstrated in Fig. 3, heat transfer occurs almost instantly relative to the mass transfer (these are plotted against the square root of time since these should be initially linear in the absence of convection). The thermal diffusivity determined from the heat transfer curves in the different gels ranged from  $2.3 \times 10^{-3}$  to  $3.0 \times 10^{-3}$  cm<sup>2</sup>/s (increasing with temperature), roughly 4 orders of magnitude greater than the mass diffusivity. Thus, the gel extraction cycle for dewatering coal slurries should not be influenced significantly by the rate of heat transfer. The rate-limiting step for the process

is clearly mass transfer, not heat transfer, and thus further work was focused on this point.

### Mass Transfer

Dimensional dependence of the volume changes is important to confirm that diffusion is the transport mechanism and also to enable designing and scaling up a gel extraction unit. From experimental data, a plot of  $M_t/M_\infty$  against  $\sqrt{t/L}$  ( $M_t$  = mass sorbed at time  $t$ ,  $M_\infty$  = mass sorbed at equilibrium,  $t$  = time, and  $L$  = initial thickness) was constructed. Theory for diffusion predicts that for a system governed by diffusion, this plot should yield a single curve for a system of any thickness,  $L$  (11, 14). In Fig. 4 the experimental data from two kinetics experiments yielded nearly the same curve for thicknesses  $L = 0.1$  cm and  $L = 0.18$  cm, and thus the same diffusivities within experimen-

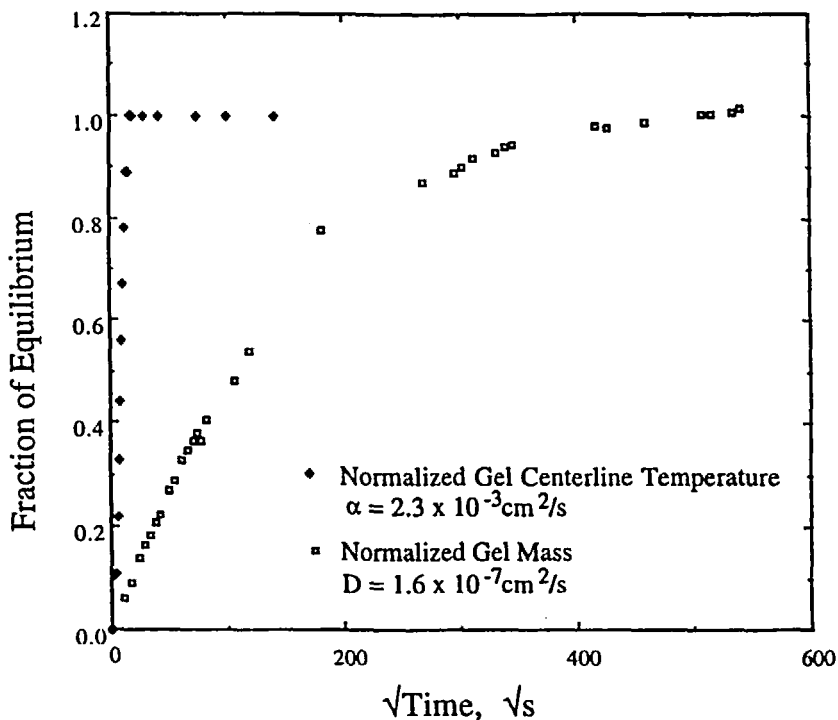


FIG. 3 Heat transfer occurs at a rate four orders of magnitude faster than mass transfer, as shown in this plot of dimensionless temperature change and dimensionless mass change against time. The gel is  $16 \times 1$  PNIPA being heated from 27 to 35°C.



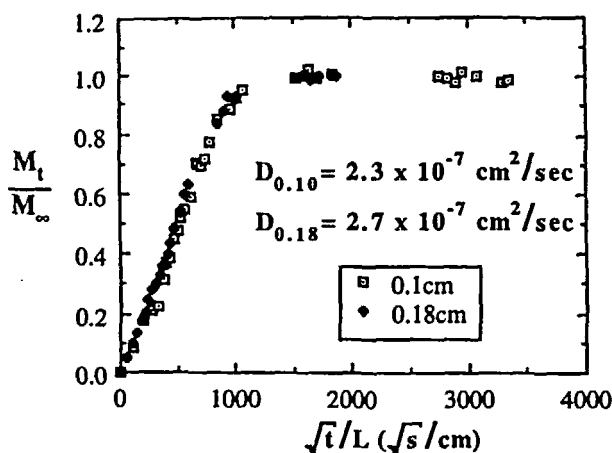


FIG. 4 Diffusion is confirmed as the rate-controlling mechanism for mass transfer, due to the initial linearity of the fractional approach to equilibrium ( $M_t/M_\infty$ ) against the square root of time and the overlap of data for different dimensions. The diffusion coefficients obtained from a fit of the exact solution of Fick's law to these curves agree within experimental accuracy.

tal error, providing further evidence that diffusion is indeed the rate-limiting transport mechanism.

In the actual gel extraction process, the gel must swell and shrink in a cycle. So the experiments were designed to let gels equilibrated at 25°C swell or shrink at 10, 15, 20, 25, 30, 32, 35, and 37°C. The reverse experiment was also performed. From the data gathered, plots of  $M_t/M_\infty$  against  $\sqrt{t/L}$  were constructed; a nonlinear least-squares method was used to determine the best-fit diffusion coefficient from the exact solution for Fick's law applied to a flat sheet (11, 14). The results are summarized in Figs. 5 and 6. It was noted that the diffusion equation did not fit the swelling and shrinking data exactly when the volume change occurred across 33°C, the transition temperature. Under these conditions the swelling curve appeared slightly sigmoidal when plotted against the square root of time; however, the best-fit diffusion coefficient reported in these cases still gave a reasonable representation of the swelling rate (11). However, when shrinking occurred by heating across this transition, the diffusion curve fit well for about the first 80% of the volume change (reflected by the value of  $D$  reported in Figs. 5 and 6), but then a second, slower stage prevailed for the final 20% of the shrinking process. Due to the presence of this second stage, possibly due to the formation of a polymer-dense skin on the surface, equilibrium takes notably longer to reach than predicted by Fick's law using the diffusion coefficients reported in the

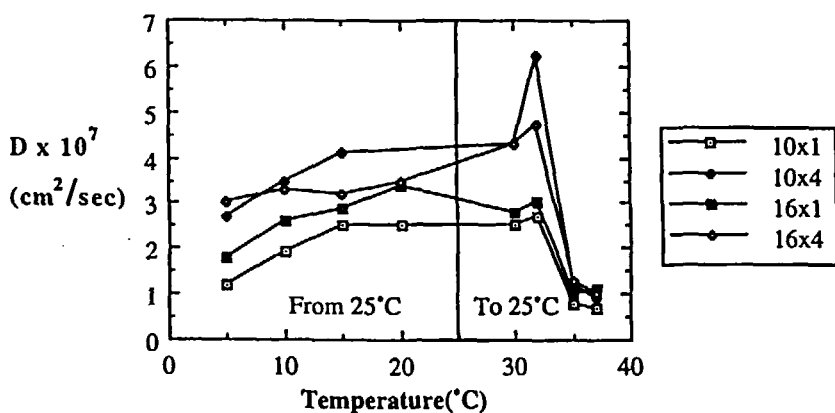


FIG. 5 The diffusion coefficients for the swelling of gels. The values of  $D$  to the left of  $25^\circ\text{C}$  started at  $25^\circ\text{C}$  and swelled at the temperature indicated on the abscissa; the values of  $D$  to the right of  $25^\circ\text{C}$  started at the temperature indicated on the abscissa and swelled to  $25^\circ\text{C}$ . The values above  $33^\circ\text{C}$  are only approximations, as Fick's law is not obeyed when the transition temperature is crossed.

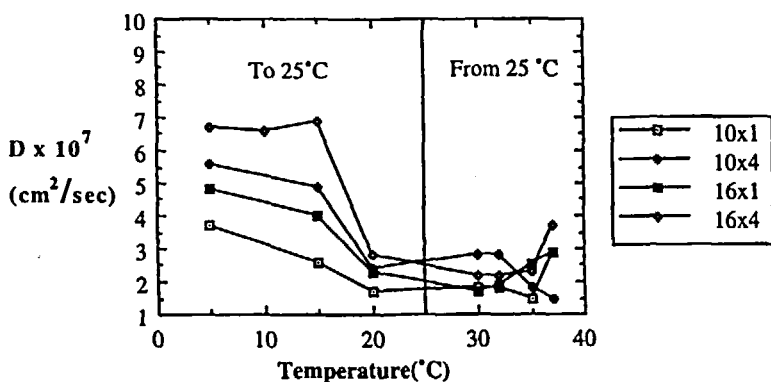


FIG. 6 The diffusion coefficients for the shrinking of gels. The values of  $D$  to the left of  $25^\circ\text{C}$  started at the temperature indicated on the abscissa and shrank to  $25^\circ\text{C}$ ; those to the right of  $25^\circ\text{C}$  started at  $25^\circ\text{C}$  and shrank to the temperature indicated on the abscissa. The values above  $33^\circ\text{C}$  are only approximations, as Fick's law is not obeyed when the transition temperature is crossed.

figures. These effects are examined in terms of polymer science theory elsewhere (11, 16, 17). In this report we focus on the use of this kinetic information in selection of gels and operating characteristics.

In Fig. 5, diffusion coefficients rise up to a factor of 2 as the temperature increases. However, swelling occurs more slowly when it occurs across the transition temperature. The values of  $D$  tend to be larger for the more densely crosslinked, lower-swelling gels than for gels of lower crosslinking and higher swelling. This also holds in the case of shrinking, as shown in Fig. 6. Shrinking also occurs more rapidly than swelling, averaging roughly twice the magnitude of those of swelling, apart from the final, slow stage observed when shrinking occurs across the transition temperature, as described above. These observations are consistent with polymer scaling theory (17).

While the full interpretation of these results is beyond the scope of this work, there are clear implications for operation of gel extraction units. First of all, maximizing the overall dewatering rate will require a complex optimization of swelling degrees in the swollen and shrunken states, swelling and shrinking rate, and temperature interval. The equation governing the amount of gel required to remove water from a slurry at a given rate  $R_w$  is

$$M_g = R_w \Theta / (q_L - q_H) \quad (1)$$

where  $M_g$  = mass of gel, dry basis (kg)

$R_w$  = water removal rate (kg/h)

$\Theta$  = cycle time (h)

$q_L$  = swelling degree at low temperature (swollen gel mass/dry gel mass)

$q_H$  = swelling degree at high temperature (shrunken gel mass/dry gel mass)

Gels with large differences in swelling degrees are desirable in terms of absorbing the maximum amount of water per unit mass of polymer, but these reach equilibrium more slowly than the lower swelling gels. Thus sorption and desorption rates in terms of water uptake per unit time will be a function of both  $D$  and  $q$ . Furthermore, the swelling and shrinking cycles will be asymmetric due to the different diffusion coefficients observed for the different legs on each cycle. Finally, changes in the temperature cycle, caused by variations in ambient temperature or heating/cooling supplied to the system, will alter not only the amount of water absorbed or desorbed (as described by Fig. 1) but also the rate of approach to equilibrium. However, the fact that swelling and shrinking generally obey Fick's law quite well means that scale-up of the process will be straightforward. For example, since the rates of volume change are diffusion-limited, equipment design must minimize the

characteristic dimensions of the gels used, since time is shown to scale with the square of the dimension. Reducing gel dimensions has a practical limit in that as gel particles become smaller, they become more difficult to separate from the slurry (5–8). But gels might also be used as thin sheets which can respond quickly yet be easily removed from the slurry (23, 24). Finally, the observation that swelling and shrinking across the transition occurs much slower than normal diffusion means that crossing the transition temperature of 33°C should be avoided, though this means sacrificing some of the possible volume change.

From the data it appears that the optimal dewatering rate (in terms of water volume per unit time) will be achieved in the 10–30°C range with a moderately crosslinked gel that will be a compromise between speed gained with a high crosslink density and increased swelling ratio from a low crosslink density. One basis for estimating the best combination of sorption capacity and speed is the time needed for a gel to process 100 times its weight in water using the sorption/desorption cycle between 25 and 32°C. These estimates are presented in Table 1, which indicates that the 10 × 4 gel is the best gel; thus this gel was used in the tests of gel extraction described below.

The processing times seem quite slow. However, microporous, temperature-sensitive gels have been developed which swell and shrink over 1000 times faster than these conventional, nonporous gels (6, 7, 17, 20–22). The results of this current project are still needed to determine what potential gel extraction has and whether simply increasing the rates could be sufficient for profitable operation. But it may also be possible to use the PNIPA gels described in this paper and cut short the shrinking cycle by avoiding use of the entire shrinking cycle, thus avoiding the slow stage that occurs for the final 20% of the weight loss. Kabra et al. describes such a concept for a different gel system (11).

TABLE 1  
Number of Cycles and Times for PNIPA Gel  
to Process 100 Times Its Dry Weight in Water<sup>a</sup>

Gel	Cycles	Time (day)
10 × 1	10	7.3
10 × 4	15	5.5
16 × 1	14	8.9
16 × 4	20	10.0

<sup>a</sup> Cycles and times determined from data in Figs. 5 and 6 for 1 mm thick gels.

## Extent and Speed of Slurry Dewatering

### *Extent of Dewatering*

A key concern for evaluation of gel extraction for dewatering slurries is how much water can be removed from the slurry; what is the final solids content? Factors involved include the initial slurry solids content, the gel swelling ratio, and the relative amount of gel and slurry. Experimental evidence also suggests that the particle size distribution also affects the dewatering capability of gel extraction.

Based on the results of the previous section, the  $10 \times 4$  gel was chosen for use in the dewatering tests. Gel sheets about 1 mm thick, shrunk to equilibrium at 32°C, were immersed in slurries at 25°C and allowed to swell to equilibrium. Experiments summarized in Fig. 7 show that gel extraction worked quite well over a variety of slurry concentrations, mesh sizes, and gel/slurry ratios. Increasing the amount of gel relative to the slurry increased the final solids content, and more coarse slurries could be dewatered to greater extents. However, plateaus were reached once the slurry became less fluid, above a solids content of about 50–60%. The primary reason for this decline is the reduction in swelling ability of the gel in the slurry, as shown in Fig. 8. Together, Figs. 7 and 8 show that the point where the final solids content levels off corresponds to the point where the swelling ratio declines sharply. It can also be seen that the finer coals cause deswelling at lower solids contents than the coarser coals. However, the errors associated with the measurements are relatively large. Thus, to confirm the deswelling effect, the gels were placed in large excesses of slurry so that the concentration of the slurry could be assumed constant. Figure 9 shows clearly that the swelling ability of the gel declines sharply above 60% solids, consistent with the results in Fig. 8, although for the size fractions tested, less significant differences were observed for different mesh sizes. Since the swelling of gels declines as solids content increases, it is expected that there will always be a maximum achievable solids content. Figure 7 supports this, where the maximum solids content achievable in a coarse –16 mesh slurry is around 80%, falling to the low 60s for ultrafine coals below 200 mesh.

It is evident that to increase the dewatering effectiveness of gel extraction, the deswelling of the gels in the slurry must be addressed. Coal slurry viscosities have been shown by Casassa to increase rapidly above 60 to 70% solids (18). A rapid increase in viscosity cannot, however, be the reason for the decline in swelling degree with increasing solids content, since viscosity is a transport property and swelling degree is an equilibrium property. It is conceivable that in a coal slurry of high solids content, the migration of water could be so slow that equilibrium could not be reached in a reasonable time. This, however, still would not explain why gels were observed to deswell

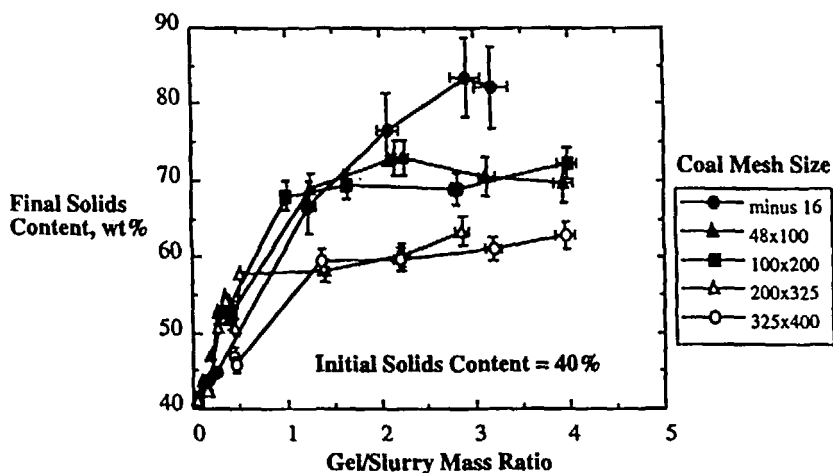


FIG. 7 The final solids content rises as the initial ratio of gel to slurry increases. The maximum extent of dewatering declines as the particles become finer. In this experiment,  $10 \times 4$  PNIPA gel at  $32^\circ\text{C}$  is added to slurry at  $25^\circ\text{C}$ . Source: Reference 17. Reprinted with permission.

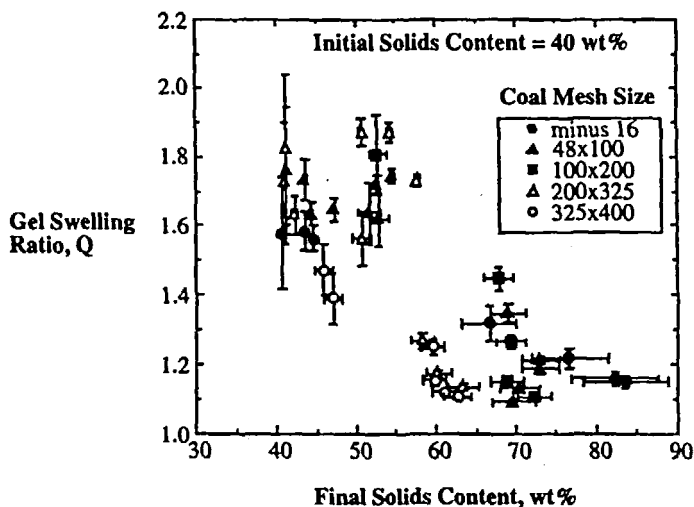


FIG. 8 The gel swelling ratio declines as the final, dewatered solids content increases. The sharp decline above 60 wt% coincides roughly with the conversion of slurries from fluid to semisolid mixtures. This decline in sorption ability of the gel is responsible for the declining dewatering ability of the gels at high solids content shown in Fig. 7. This effect appears to be more pronounced for sub-200 mesh coal particles. Swelling ratio is the ratio of initial gel mass to final gel mass.

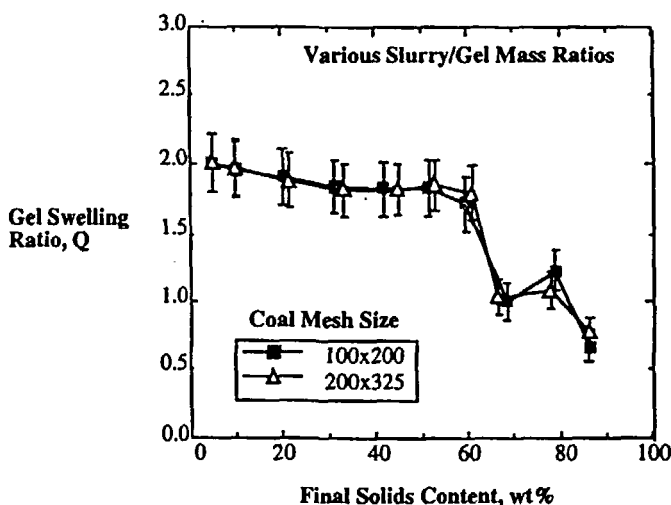


FIG. 9 The gel swelling ratio declines at slurry solids contents greater than 60% for the finer coal slurries. This confirms the observations in Fig. 8 which were obtained in dewatering experiments. In contrast, these experiments used a large excess of slurry, thus minimizing error in measurements of slurry concentration.

when placed in very high solids content slurry ( $>80\%$ ), as seen in Fig. 9. Instead, we consider the fact that water adsorbs onto the surface of coal in these in concentrated coal slurries. This surface water may have a lower chemical potential than bulk water; it is known that water adsorbed to hydrophobic surfaces has different thermodynamic properties than free water (17). For equilibrium to exist, the chemical potential of the water in the gel must be equal to the chemical potential of water in the slurry. Since the chemical potential of the water rises as the swelling degree rises, if the chemical potential of the water in the slurry falls with increasing solids content, then so must the swelling of the gel.

Since vapor pressure is directly related to chemical potential, it was possible to test this hypothesis by measuring the vapor pressure of slurries of various solids contents. In this simple experiment, slurries were put into an evacuated Erlenmeyer flask, and the pressure inside the flask was measured once equilibrium had been established. Results showed clearly that vapor pressure fell sharply between 50 and 60% solids, to about half that of pure water, for both  $48 \times 100$  and  $200 \times 325$  slurries. This is the same range over which the swelling degree drops. Theoretically, this hypothesis implies that the drop in swelling degree should occur at lower solids contents for slurries of finer

coal particles, as observed in Figs. 8 and 9. The experimental measurements of vapor pressure were insufficiently accurate to confirm this hypothesis, however. Because this is a thermodynamic limitation on gel swelling, it appears that gel extraction cannot be optimized to dewater slurries to much greater than the range of 60–80% solids.

### *Kinetics of Gel Volume Change in Coal Slurries*

It has been shown thus far that gel extraction can dewater slurries quite effectively to solids contents over 60%, even for the finest particles. Thus it seems that the relatively slow kinetics of swelling and shrinking remain the biggest obstacle for commercial development of gel extraction. It is important to determine the effect that the presence of coal in the fluid may have on the sorption/desorption kinetics. Specifically, we wished to determine whether the adsorption of coal to the gel surface affects kinetics, whether the slurry concentration affects kinetics, and whether the possible rate-limiting transport of water through a high solids content bed will alter swelling or shrinking rates. Experimental data recorded in Table 2 provide answers to the first questions. In these experiments the gels were cycled between 25 and 32°C. In all cases the kinetics curves matched Fick's law quite well, allowing calculation of a diffusion coefficient for each case. It appears that simply coating

TABLE 2  
Diffusion Coefficients of Swelling and Shrinking PNIPA Gels in Water and Coal Slurry  
Between 25 and 32°C

Test medium	Gel state	Swelling ratio (initial mass: final mass)	Diffusion coefficient ( $10^7 \text{ cm}^2/\text{s}$ )
<b>Swelling cycles:</b>			
Water	Clean	1.85	5.7
Water	Coal-coated	1.57 <sup>a</sup>	3.4 <sup>a</sup>
20 wt% 48 × 100 mesh slurry	Coal-coated	1.50 <sup>a</sup>	3.3 <sup>a</sup>
40 wt% 48 × 100 mesh slurry	Coal-coated	1.47 <sup>a</sup>	3.5 <sup>a</sup>
70 wt% 48 × 100 mesh slurry	Coal-coated	1.30	3.7
<b>Shrinking cycles:</b>			
Water	Clean	0.53	2.8
Water	Coal-coated	0.57 <sup>a</sup>	2.7 <sup>a</sup>
20 wt% 48 × 100 mesh slurry	Coal-coated	0.52	1.8
40 wt% 48 × 100 mesh slurry	Coal-coated	0.50	1.9
70 wt% 48 × 100 mesh slurry	Coal-coated	0.41 <sup>b</sup>	1.9 <sup>b</sup>

<sup>a</sup> Averages of two trials.

<sup>b</sup> Average of three trials.



the gels with coal does cause the swelling rate to decline, although the shrinking rate is little affected. Increasing the solids content, even up to 70% solids, has a negligible effect upon kinetics although the swelling degree does decline.

If transport of water through the slurry bed was rate-limiting, the disturbance and mixing caused by removing a gel sample and then returning it to the slurry would destroy such an effect. To avoid this, a series of 25 identical slurries were prepared, and into each a piece of gel was immersed. The samples were removed at different times and weighed so that a kinetics curve of 25 points could be constructed. The experiment was difficult to perform, however, and the results could not be evaluated quantitatively. It was nonetheless observed that the gels swelled and shrank at typical rates under these circumstances. Thus, it does not appear that water transport through the slurry is rate-limiting.

### Service Lifetime of PNIPA Gel

The results of this experiment were very positive; the gel's properties were found to be exceedingly stable, and no deterioration or variation in performance with cycle number was observed. Degrees of swelling, in both swollen and shrunken states, remained constant within experimental error in both water and coal slurry over a 2-month, 21 cycle test period. After 20 cycles of swelling and shrinking, the swelling and shrinking kinetics were measured and found to have remained unchanged. The swelling ratios also remained constant as shown in Fig. 10. Clearly, the repeated swelling and shrinking cycles do not in and of themselves cause deterioration or other changes in gel properties. This shows that no special precautions are necessary to preserve gels, beyond careful handling of the samples when in the fully swollen state. Similarly, good stability of a different type of reversibly swelling and shrinking gel was reported by Kryuchkov (19).

It was also observed that no abrasive degradation occurred in the gels after 1 week of exposure to moving coal slurry. Regardless of sample orientation (parallel or perpendicular to slurry flow) or agitation, the gels remained intact and unchanged. This does not mean that gels are resistant to any sort of abrasive action, but that abrasive degradation should not be a concern under normal circumstances.

### Practical Considerations

It is worthwhile to consider the implications of these results with regard to development of a practical gel extraction unit. The results obtained in this work indicate both where such a unit could be used in a slurry dewatering process and provide guidelines for the design of such a unit. In terms of

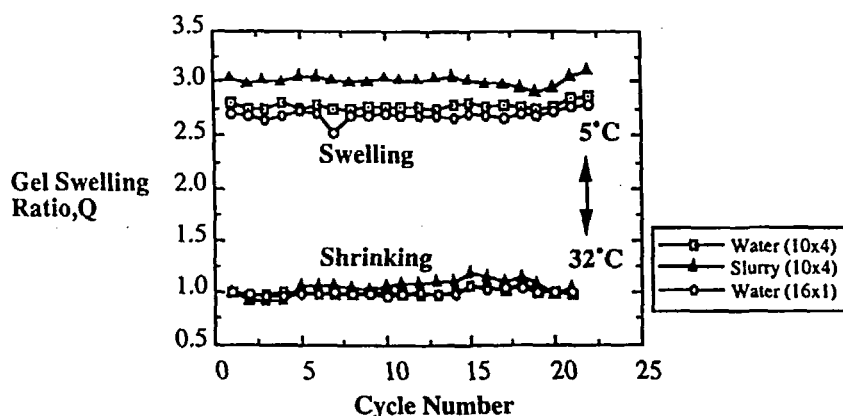


FIG. 10 The properties of PNIPA gels are stable after numerous reuses. In this figure the swelling ratios (mass of gel relative to initial mass at 32°C) of the gel in water and slurry repeatedly return to the original values of 3.0 and 1.0 for swelling and shrinking, respectively. Also, the swelling and shrinking kinetics of the final cycle were the same as the initial cycle.

dewatering ability, gel extraction does not match the performance of the centrifuge (which can reach 85% solids) but meets or exceeds the values achieved by other dewatering alternatives, such as static thickeners (up to 30% solids), dewatering screens (up to 75% solids), or disk filters (up to 75% solids). While gel extraction exceeds the performance of the static thickener, its equipment design, operation, and costs are more likely to be in the range of that of dewatering screens or filters. Thus gel extraction is most likely to compete with dewatering screens and disk filters since the product quality is comparable.

Different designs for a practical gel extraction unit have been envisioned, but the viability of any design hinges on the reusability of the gel, since the costs of regeneration of the gel using waste heat will be negligible (6, 8, 23). Earlier in the paper, the  $10 \times 4$  PNIPA gel cycling between 25 and 32°C was identified as having the best combination of a relatively short cycle time with a relatively large difference in swollen and shrunken swelling degree ( $q_L - q_H$ ), thus reducing the amount of gel required to dewater at a given rate. But the largest problem with PNIPA is the slow swelling and shrinking kinetics. Because of the slow swelling and shrinking rates, the cycling time is quite long. Therefore, a large amount of PNIPA gel and associated equipment must be purchased in order for the overall dewatering rate to meet the needs of the slurry production rate. However, with the fast-response gels described, the capital and gel costs fall dramatically. This response can be

achieved by synthesizing responsive gels with a microporous, sponge-like structure that allows the gel to absorb and desorb water by a convective process which is much faster than the slow diffusive process undergone by the homogeneous PNIPA gel (20–22). In fact, we have estimated that the costs associated with dewatering by gel extraction drop more than an order of magnitude if fast-response gels are used (24).

Gel extraction may prove to be much more reliable and effective for feeds of variable fines content or ultrafine slurries in terms of dewatering rates. As seen before, the kinetics of gel extraction are seemingly unaffected by particle size. Also, there is no tendency in gel extraction for the ultrafines to blind the filtration surface, as often happens with disk filters. Furthermore, it may be anticipated that these results will apply to the dewatering of any slurry comparable in characteristics to coal slurries. Also, other temperature-responsive gels which can be synthesized from commodity polymers like cellulose ethers should display similar dewatering performance to PNIPA while being potentially much cheaper materials (12, 25). In conclusion, gel extraction has potential to be a viable alternative to current methods of dewatering a variety of slurries.

## CONCLUSIONS

We have acquired quantitative and qualitative knowledge that provides a sound basis for evaluating and developing gel extraction as a feasible alternative to the current methods of slurry dewatering. We have established that gel extraction is capable of dewatering fine coal slurries as small as 400 mesh to an extent comparable to vacuum disk filtration and dewatering screens. Furthermore, gel properties are stable with time; no deterioration was observed from repeated absorption/desorption cycles or from contact with coal slurry. Particularly with continued development of fast-response gels, gel extraction has significant promise as a means of slurry dewatering.

## ACKNOWLEDGMENTS

This project was supported by the Ohio Coal Development Office (Grant Agreement CDO/R-87-57). Huajie Zhu assisted with preparation of the manuscript.

## REFERENCES

1. E. L. Cussler, M. R. Stokar, and J. E. Varberg, "Gels as Selective Extraction Solvents," *AIChE J.*, **30**, 578 (1984).
2. S. H. Gehrke, G. P. Andrews, and E. L. Cussler, "Chemical Aspects of Gel Extraction," *Chem. Eng. Sci.*, **41**, 2153 (1986).

3. S. H. Gehrke and E. L. Cussler, "Mass Transfer in pH-Sensitive Hydrogels," *Ibid.*, **44**, 559 (1989).
4. R. F. S. Freitas and E. L. Cussler, "Temperature Sensitive Gels as Extraction Solvents," *Ibid.*, **41**(1), 97 (1987).
5. H. Ichijo, R. Kishi, and O. Hirasa, "Separation of Organic Substances with Polymer Hydrogel," *Polym. Gels Networks*, **2**, 315 (1994).
6. X. Huang, A. Takashi, H. Unno, and O. Hirasa, "Dewatering of Biological Slurry by Using Water-Absorbent Polymer Gel," *Biotechnol. Bioeng.*, **34**, 102 (1989).
7. O. Hirasa, *Polym. Prepr. (Japanese)*, **36**, 2952 (1987).
8. P. Y. Huang, Y. Tsao, and M. E. Ublehor, US Patent 5,258,123 (1993).
9. S. H. Gehrke, M. Palasis, and M. K. Akhtar, "Effect of Synthesis Conditions on Properties of Poly(*N*-Isopropylacrylamide) Gels," *Polym. Int.*, **29**, 29 (1992).
10. B. Kabra, S. H. Gehrke, S. T. Hwang, and W. Ritschel, "Modification of the Dynamic Swelling Behavior of PHEMA," *J. Appl. Polym. Sci.*, **42**, 2409 (1991).
11. B. Kabra, M. K. Akhtar, and S. H. Gehrke, "Volume Change Kinetics of Temperature-Sensitive Poly(Vinylmethylether) Gel," *Polymer*, **33**, 990 (1992).
12. D. C. Harsh and S. H. Gehrke, "Controlling the Swelling Characteristics of Temperature-Sensitive Cellulose Ether Hydrogels," *J. Contr. Rel.*, **17**, 175 (1991).
13. D. C. Harsh and S. H. Gehrke, "Characterization of Ionic Water Absorbent Polymers: Determination of Ionic Content and Effective Crosslink Density," in *Absorbent Polymer Technology* (L. Brannon-Peppas, Ed.), Elsevier, Amsterdam, 1990, pp. 103-124.
14. S. H. Gehrke, D. Biren, and J. Hopkins, "Evidence for Fickian Water Transport in Initially Glassy Poly(2-Hydroxyethyl Methacrylate)," *J. Biomater. Sci., Polym. Ed.*, **6**, 375 (1994).
15. S. Saito, M. Konno, and H. Inomata, "Volume Phase Transition of *N*-Alkylacrylamide Gels," *Adv. Polym. Sci.*, **109**, 207-232 (1993).
16. E. S. Matsuo and T. Tanaka, "Kinetics of Discontinuous Volume-Phase Transitions of Gels," *J. Chem. Phys.*, **89**(3), 1695 (1988).
17. S. H. Gehrke, "Synthesis, Equilibrium Swelling, Kinetics, Permeability and Applications of Environmentally Responsive Gels," *Adv. Polym. Sci.*, **110**, 81-144 (1993).
18. E. Z. Casassa, G. D. Parfitt, A. S. Rao, and E. W. Toor, "Rheology of Coal/Water Slurries," *Coal Slurry Combustion 5th Symposium*, **2**, 1205 (1982).
19. F. A. Kryuchkov, "Degradation of Polymer Hydrogel in the Course of Cyclic Volume Changes," *Polym. Sci. Ser. A*, **37**(6), 651 (1995).
20. B. Kabra and S. H. Gehrke, "Rate Limiting Steps for Solvent Sorption and Desorption by Microporous Stimuli-Sensitive Absorbent Gels," in *Superabsorbent Polymers: Science and Technology* (ACS Symposium Series 573), (F. L. Buchholz and N. A. Peppas, Eds.), Washington, D.C., 1994, pp. 76-87.
21. B. Kabra and S. H. Gehrke, "Synthesis of Fast Response Poly(*N*-Isopropylacrylamide) Gels," *Polymer Commun.*, **32**, 322-323 (1991).
22. B. Kabra, S. H. Gehrke, and R. Spontak, "Microporous Responsive HPC Gels 1. Synthesis and Microstructure," *Macromolecules*, **31**, 2166-2173 (1998).
23. E. L. Cussler, K. L. Wang, and J. H. Burban, "Hydrogels as Separation Agents," *Adv. Polym. Sci.*, **110**, 67-79 (1993).
24. S. H. Gehrke and L. H. Lyu, *Dewatering Fine Coal Slurries by Gel Extraction*, Ohio Coal Development Office Reports, Columbus, OH, 1990.
25. S. M. O'Connor and S. H. Gehrke, "Synthesis and Characterization of Thermally-Responsive Hydroxypropylmethylcellulose Gel Spheres," *J. Appl. Polym. Sci.*, **66**, 1279-1290 (1997).

Received by editor September 17, 1997

Revision received November 11, 1997