TECHNICAL PROGRESS REPORT

APPALACHIAN CLEAN COAL TECHNOLOGY CONSORTIUM

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Project Report for the period

July 1 - September 30, 1996

Performing Organizations:

Virginia Polytechnic Institute & State University
Blacksburg, VA
R.-H. Yoon, D.I. Phillips, G.H. Luttrell, B. Basim, S. Sohn

University of Kentucky
Lexington, KY
X. Jiang, D. Tao, and B. K. Parekh

West Virginia University
Morgantown, WV
T. Meloy

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Contracting Officer's Representative: Richard Read

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Introduction

The Appalachian Clean Coal Technology Consortium (ACCTC) has been established to help U.S. Coal producers, particularly those in the Appalachian region, increase the production of lower-sulfur coal. The cooperative research conducted as part of the consortium activities will help utilities meet the emissions standards established by the 1990 Clean Air Act Amendments, enhance the competitiveness of U.S. coals in the world market, create jobs in economically-depressed coal producing regions, and reduce U.S. dependence on foreign energy supplies.

The consortium has three charter members, including Virginia Polytechnic Institute and State University, West Virginia University, and the University of Kentucky. The Consortium also includes industry affiliate members that form an Advisory Committee. Affiliate members currently include AMVEST Minerals; Arch Minerals Corp.; A.T. Massey Coal Co.; Carpco, Inc.; CONSOL Inc.; Cyprus Amax Coal Co.; Pittston Coal Management Co.; and Roberts & Schaefer Company.

Objectives

In keeping with the recommendations of the Advisory Committee, first-year R&D activities were focused on two areas of research: fine coal dewatering and modeling of spirals. The industry representatives to the Consortium identified fine coal dewatering as the most needed area of technology development. Dewatering studies were conducted by Virginia Tech's Center for Coal and Minerals Processing and a spiral model was developed by West Virginia University. For the University of Kentucky the

advisory board approve a project entitled: "A Study of Novel Approaches for Destabilization of Flotation Froth". Project management and administration will be provided by Virginia Tech, for the first year.

Innovative Approaches to Fine Coal Dewatering
Virginia Tech

R.-H. Yoon, D.I. Phillips, G.H. Luttrell, B. Basim, S. Sohn

Introduction

There are no practical solutions to the problems associated with the dewatering of fine coals at the moment. The mechanical dewatering technologies used today are inefficient while thermal drying is capital-intensive and costly to operate. Therefore, there is an impending need for innovative approaches to solving problems in fine coal dewatering.

In this project, two different approaches are taken. One approach involves displacing the water on the surface of coal by liquid butane that can be readily recovered and recycled. The other approach is to use disposable dewatering chemicals (aids) in mechanical dewatering.

The objectives of the proposed work are i) to test the liquid butane process on a variety of coals from the Appalachian coal fields, and ii) to identify suitable dewatering aids that would enable mechanical dewatering to reduce the moisture to the levels satisfactory to electrical utilities and other coal users.

Dewatering Using Liquid Butane

Test results obtained using the liquid butane dewatering process have been described in previous reports. During the past quarter, most of the research work was done on testing dewatering aids.

Use of Dewatering Aids

A series of vacuum filtration tests were conducted on a variety of bituminous coals using various dewatering aids developed at Virginia Tech. The nature of the reagents are not disclosed here due to the proprietary nature. The tests were conducted using a 3-inch diameter Buchner funnel with a medium porosity. In each test 100 to 200 ml of coal slurry was poured into the funnel before a vacuum pressure was applied. The various parameters investigated in this quarter were pressure, drying cycle time, and temperature.
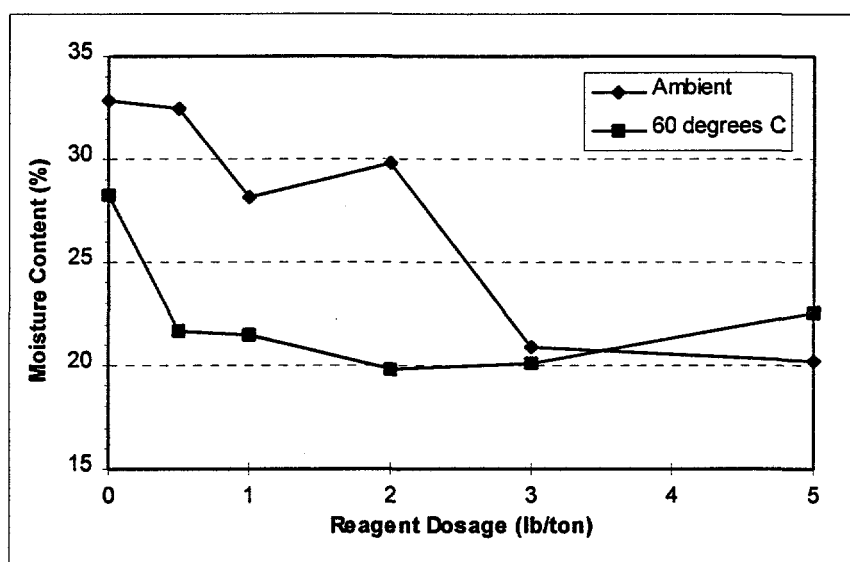

Figure 1. Moist content at different reagent dosages and temperature on a -100 mesh Pittsburgh #8 coal sample.

It is well known that increasing the temperature of the coal feed to a vacuum filter will decrease the moisture content of the product. A -100 mesh sample of Pittsburgh #8 coal was tested at ambient temperature (23° C) and at an elevated temperature of

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60°C. As shown in Figure 1, the moisture was initially lower for the increased temperature, but as the dosage of reagent was increased to 3 lb/ton the ambient temperature moisture contents were as low as those using higher temperatures.

The final economics of the dewatering aids is not known yet but preliminary estimates indicate that reagent consumptions up to 3 pounds per ton of coal are in the economically viable range. Figure 2 shows that 3 different reagents can reduce the moisture by up to 10 percentage points on an Elkview coal sample at reagent dosages of up to 3 lb/ton.
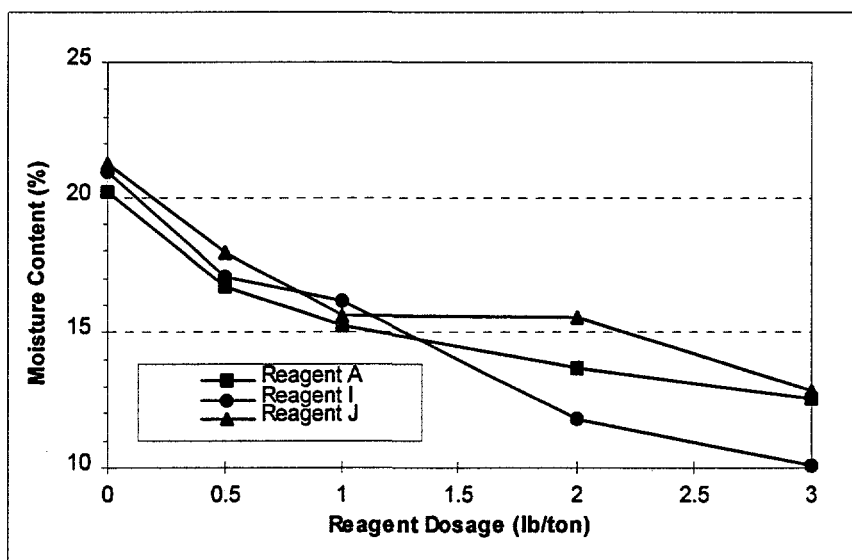

Figure 2. Moisture contents for three separate reagents on Elkview coal sample.

The length of time that a sample is exposed to a vacuum will obviously affect the final moisture content. To better assess this effect and to determine the general range of drying cycle time to use in testing, a series of tests were performed at different drying cycle times using no reagent. The vacuum pressure was varied from 15 to 25 inches of mercury to determine the effect of vacuum on the moisture content. As shown in Figure

3, the drying cycle time has an effect up to 5 minutes. The benefit from increased drying time is much more pronounced for the lower vacuum (15 inches) than for the higher vacuum (25 inches). At a fixed drying time of 3 minutes, testing was performed to determine if the vacuum pressure had much effect when using reagent. Figure 4 shows that at the lower reagent dosages, the higher vacuum still produces lower moisture contents but at dosage of 2 lbs/ton the moisture contents are similar.
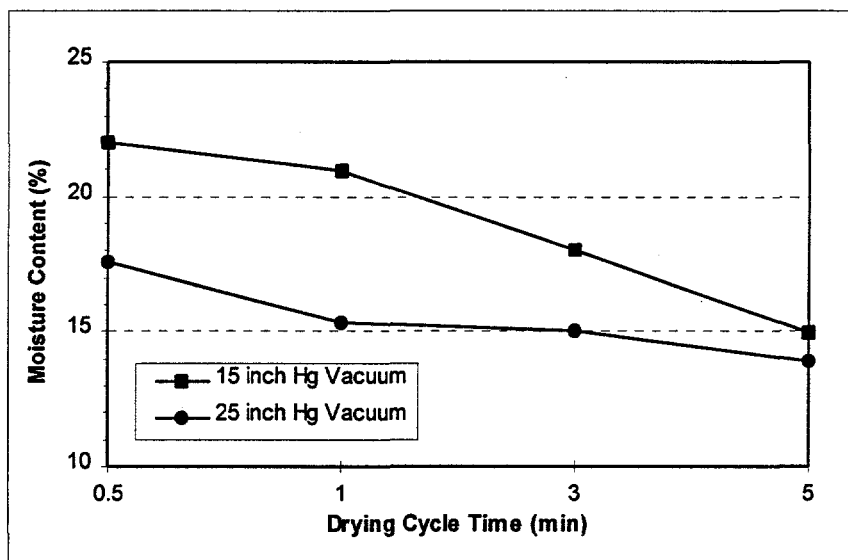

Figure 3. Effect of drying cycle time and vacuum pressure on moisture content with no reagent.

A fine coal sample was also obtained from the Amax R&D Premium Fuels project in Golden, Colorado. The sample was an Indiana 7 seam coal that had been finely pulverized in a ball mill. Both reagent A and E were unsuccessful at dewatering these samples. The base moisture obtained without any dewatering aid was 51% using bench scale vacuum filtration. With the addition of two different dewatering aids (separate tests) the moistures did not improve at all, even at relatively high dosages. Due to the very fine size consist of the sample, a high reagent dosage would be

expected. However, since the high dosages used (10 lb/ton) gave no improvement in moisture, one can only assume that the sample had severely oxidized.
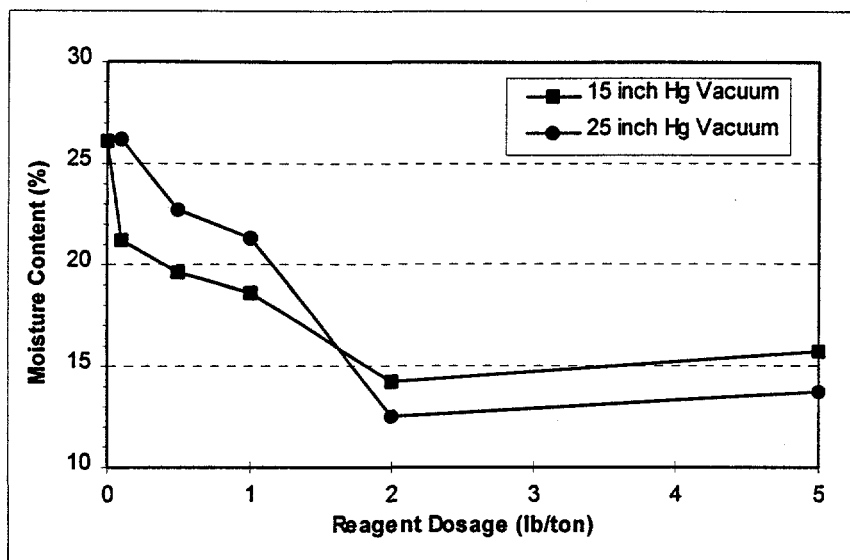

Figure 4. Effect of Reagent A dosage and vacuum pressure on moisture content.

Although testing continues, much has been learned about the relationships of vacuum dewatering with the use of a dewatering aid. It is becoming more apparent that the methodology of performing dewatering tests with a laboratory unit is crucial to consistent results. The nature of the coal surface itself also plays a role when using dewatering aids. Successful results have been obtained with the use of specific dewatering aids but more must be learned about the interrelationships and effects of the other physical dewatering parameters.

Spiral Concentrator Modeling
West Virginia University

T. Meloy

The spiral modeling is complete and all project goals were met. The final report is in progress.

Quarterly Technical Progress

Report 4

July-September, 1996

STUDY OF NOVEL APPROACHES FOR

DESTABILIZATION OF FLOTATION FROTH

By

X. Jiang, D. Tao, and B.K.Parekh

Center for Applied Energy Research
University of Kentucky
Lexington, KY 40511

October 4,1996

STUDY OF NOVEL APPROACHES FOR

DESTABILIZATION OF FLOTATION FROTH

ABSTRACT

Fine coal recovery from fine waste stream using froth flotation technique is becoming an important and integral part of coal preparation plans. Column flotation technique has proven to be the most effective and cost-efficient in recovery of fine coal. However, in some columns use of glycol-based frother produces a stable froth, which is not destroyed easily. The main objective of this program is to develop novel approaches for destabilization of stable froth. The approaches involve addition of either chemically treated coarse coal or addition of chemically treated magnetite-limestone suspended in an oil medium to the froth to break it down. Mechanical approaches to be tested involve utilization of ultrasonic energy or cyclone or vacuum. This report discusses technical progress made during the quarter from January to March 1996.

INTRODUCTION

In froth flotation process, frothers are utilized to produce stable small bubbles which carry the floatable particle. In case of an ideal froth flotation, the froth should have good fluidity and optimal rigidity. The froth should be just stable enough to carry the floated particles out of the flotation cell. Once the froth is scraped out the cell, it

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should collapse to free and concentrate the volume of floated particles. Such a froth will minimize the entrainment of undesired mineral particles into the concentrate and can provide additional selectivity for the flotation process. Too stable or too unstable froths penalize the separation efficiency and operation smoothness. If the froths are too stable, they will not break up after being scraped out of the flotation cell. Usually, such overly stable froths have low fluidity. The unwanted excessive stability can cause serious problems for downstream processes, such as dewatering of flotation concentrate, tailings handling, and re-use of processing water.

Generally, alcohol-based frothers provide froth which collapses as soon as froth is removed from the flotation cell and sprayed with water. Glycol-based frothers on the other hand produce a much stronger froth which is difficult to break by simple physical techniques and requires a large amount of chemicals to break the froth, which adds to the processing cost.

OBJECTIVES AND SCOPE

The main objective of the proposed project is to develop new defoaming techniques for destruction of overly stable froths produced in fine coal froth flotation. It is also the objective of the project to study chemical dynamics of the three phrase froth.

The focus of this project will be to investigate new defoaming techniques. The existing commercial defoamers, such as surfactants, copolymers, hydrophobic silica, amide particle, are expensive and thus economically unfavorable for breaking up fine

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coal froths. In this project, new techniques for defoaming coal froth with less expensive chemical will be developed. Two approaches will be studied. One will involve use of coarse coal particles. To ensure that the surfaces of coal particles are sufficiently hydrophobic, the coal particles will be pretreated with cationic surfactant. The second approach will be to use magnetite and limestone particles. Since both magnetite and limestone particles are naturally hydrophilic, it is necessary to coat the particles with specific chemicals to make the surface highly hydrophobic (contact angle >120°). The hydrophobic particles are then dispersed in oil. It is anticipated that these new defoamers will be advantageous over existing defoamers. Besides their low cost, the use of hydrophobic limestone particles can also help to capture the sulfur dioxide during combustion and thus reduce the mission.

APPROACH

The project consists of four (4) tasks. Progress made in each task during the period of April -June, 1996 is described below.

Task 1. Sample Acquisition and Characterization

Destabilization studies of flotation froth will be conducted with both flotation feed and froth product. Both samples have been obtained from the Pittston Coal Company which was recommended by the ACCTC. The flotation feed contains 32.93% ash and column froth product 8.54% ash. Size analysis of the feed and product samples have be performed and results included in the last quarterly report. The major findings are that D_{50} is 40 and 80 μm for the feed and product, respectively and the froth product

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contains significantly less fine particles (<75 μm) than the feed (48 vs. 63%).

Task 2. Dynamic Destability Studies of Fine Coal Froth

Experimental

Dynamic destability studies of fine coal flotation froth were performed using the principles of a "Foam Stabo System" developed at UKCAER, which was shown in the first quarterly report. Improvements were made to the original system during the second quarter to obtain reliable data on froth stability. They included:

- Replacing easy-action-plug stopcock with straight-bore-plug stopcock to reduce disturbance to the system,

- Separating both reference and working foam cells into two portions for easy cleaning of porous frit used as bubble generator,

- Connecting the pressure transducer to a computer to establish a data acquisition system.

- Attaching a small cup to the foam cell to add chemical reagents, coarse coal, magnetite and limestone particles during experiment without disturbance to the system

Experiments conducted during the last quarter indicated that the pressure measurement with the system was very sensitive to the environmental temperature. Theoretical error analysis with the froth state equation reveals that a variation of 0.1 K in temperature leads to a change of 8.31 Pa in pressure. It was, therefore, of critical importance to perform tests under controlled temperature. This was accomplished by

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utilizing a HAAKE C constant temperature bath and circulator that controls the temperature of water between the inner and outer wall of the froth column. In addition, the bubble generator in both columns has been changed to a fine frit (4-8 μm) to reduce the amount of water that may penetrate the frit after bubbling gas is turned off.

Results and Discussion

In order to calculate the surface area of froth in the working column from the measured differential pressure, the surface tension of water solution of Allied Colloids 944 B frother currently used at the Pittston Holston plant was determined as a function of frother concentration. Two different methods were employed for solution preparation: a), mixing with a magnetic stirrer for 5 minutes and b), emulsifying in a blender. The tests were conducted at 20.7 °C. The results are shown in Figure 1 over the frother concentration range of 0 to 66 ppm. As can be seen, there is a large degree of scatter among the data obtained with the solution prepared using a magnetic stirrer. On the other hand, data obtained with emulsified solution showed excellent reproducibility and the curve connecting these data points lies right in the middle of surface tension values produced with stirrer agitated solution. This indicated that emulsified frother solution must be used in forth destabilization studies to ensure data accuracy.

The CMC for this specific surfactant has also been determined. This was accomplished by measuring the surface tension of solution at different frother

concentrations up to 1000 ppm. The relationship between surface tension and frother concentration is shown in Figure 2. The CMC of this frother is determined to be approximately 80 ppm.

Figure 3 shows the differential pressure between the working column and the reference column as a function of froth drainage time. Also shown in Figure 3 is the change of surface area of froth in the working column when froth drained and destabilized. The dynamic froth was generated by bubbling solution with air for 30 seconds using different air rates. The frother, Allied Colloids 944 B, was used in tests at a concentration of 250 ppm. The differential pressure increased with time as more bubbles broke in the working column and transformed the surface free energy into pressure. When the froth collapsed completely, the pressure reached a maximum. The froth produced at higher air rate resulted in higher maximum differential pressure and required longer time to collapse. For example, at an air flow rate of 0.3 l/min the maximum pressure was 12 mm H_2O and froth collapsed in 30 seconds. When air rate was increased to 1.0 l/min, the maximum pressure increased to 42 mm H_2O and collapsing time to 40 seconds. This indicated a higher stability of froth generated at higher gas rate, which is in agreement with the previous conclusion derived from other techniques.

With the known surface tension value of the solution and the differential pressure, surface area of froth can be calculated using the equation given below,

$$A(t) = (3V/2\sigma)(\Delta P_\infty - \Delta P(t)) \tag{1.}$$

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As can be seen from Figure 3, the surface area of bubbles in the froth decreased as bubbles coalesced. The decay rate of the froth decreased with time and there appeared to be an exponential relationship between surface area of froth and froth drainage time.

Figure 4 shows changes in differential pressure and foam surface area with drainage time for the steady state froth generated with 250 ppm frother. The steady state froth was produced by bubbling solution for additional 3 minutes after the froth reached maximum height at a given air flow rate. The other conditions are the same as described above. Higher air flow rate produced higher maximum differential pressure, i.e., more stable froth and more surface area. In comparison with Figure 3, the maximum pressure and the initial surface area were higher in Figure 4 at a given air rate. This was because the steady state froth represented the maximum forth height that can be possibly achieved at a given gas rate and contained more bubbles than non-steady state froth. Increase in aeration rate generally increased froth surface area. However, less significant effect of aeration rate on surface area was observed at higher aeration rate, possibly because higher aeration rate produced larger bubble size.

Figures 5 and 6 show results obtained with dynamic and steady-state froths generated at a frother concentration of 375 ppm. The overall trend of changes in differential pressure and surface area as a function of drainage time is the same as in Figures 3 and 4. The dynamic froth at 375 ppm frother concentration generally

showed higher equilibrium pressure and higher surface area of froth than at 250 ppm concentration. This is consistent with the concept that more frother produces smaller bubbles and larger gas-liquid interfacial area. With steady-state froth, higher frother dosages generated higher equilibrium pressure and initial surface area at lower gas rates (324 and 563 ml/min), but lower equilibrium pressure at higher gas rates (786 and 1003 ml/min).

Tests were also performed using 500 ppm of frother concentration. The results are shown in Figures 7 and 8 with dynamic and steady-state froth, respectively. Differential pressure increased and surface area decreased with froth drainage time, as observed in Figures 3-6. However, it is noticed that there was much more significant difference in surface area of dynamic and steady-state froth at 500 ppm frother concentration than at lower concentrations. In addition, the decay of steady-state froth was considerably slower at 500 ppm than at lower concentrations while that of the dynamic froth at 500 ppm was not.

The time required to reach the equilibrium pressure or completely destroy the froth increased with increasing the gas rate. This is due to the fact that higher gas rate generated more bubbles and more stable froth and, therefore, longer time is needed for liquid film to drain to a critical film thickness where froth collapses. Similar behavior was observed with respect to frother concentration. Higher frother concentration produced smaller bubbles which took longer time to drain, coalesce, and finally rupture.

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To better show the relationship between froth stability and gas rate, the half-drainage time, defined as the time required for differential pressure to increase to 50% of the equilibrium or maximum value, was plotted in Figure 9 for dynamic and steady state froths produced at a frother concentration of 250 ppm. Obviously, more stable froth was obtained at higher gas rate.

Figure 10 shows the change of differential pressure and surface area of froth as a function of drainage time at different frother concentrations. Increase in the frother concentration from 125 to 375 ppm stabilized the froth. However, a frother concentration of 500 ppm produced less stable froth than 375 ppm concentration, indicating that an excessive dosage of frother is detrimental to froth generation. Although the differential pressure at 125 ppm was higher than at 500 ppm, the surface area was higher at 500 ppm than at 125 ppm, due to lower surface tension produced by higher frother concentration.

Table 1 shows the drainage constant and the half-drainage time obtained at different frother concentrations. These values were obtained by fitting the curves in Figure 10 with the exponential growth equation (2) over the differential pressure range of 0 to maximum,

$$y = a(1 - e^{-kt}). \qquad (2)$$

The most stable froth was obtained at a frother concentration of 375 ppm, as indicated by its drainage constant k and half-drainage time. The largest surface area

Table 1. Drainage constant and half-drainage time at different concentrations

Frother Concentration (ppm)	Drainage Constant (k) (1/s)	Half-Drainage Time ($t_{1/2}$) (s)
125	0.2749	2.52
250	0.2800	2.48
375	0.2455	2.82
500	0.2768	2.50

was also produced at 375 ppm. At other frother concentrations, the froth drainage constant and half-drainage time were nearly the same to each other although there was significant difference in the value of differential pressure and surface area.

Task 3. Fine Coal Froth Destabilization Studies

This task will consist of studies on chemical and mechanical defoaming techniques for fine coal flotation froth. The chemical process involves use of coal, magnetite, or limestone particles coated with surfactant for froth spraying. The mechanical process utilizes cyclone, ultrasonic energy, or vacuum to destabilize froth.

CONCLUSIONS

1.   The "Foam Stabo System" developed at UKCAER has proved to be an effective technique for studying froth stability.

2.   Effects of gas rate and frother concentration on two-phase froth have been studied using "Foam Stabo System" with Allied Colloids 944 B frother and the

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coal sample from Holston coal mine of the Pittston Coal Company.

3.   The differential pressure between the working froth column and the reference column increased almost exponentially with drainage time as froth destabilizes.

4.   Surface area of froth can be determined from the measured differential pressure. It decayed nearly exponentially during froth breakage.

5.   More stable froths were generated at higher gas rates and higher frother concentrations. However, an excessive dosage of frother destabilized froth.

6.   Data on surface area of froth produced at different frother concentrations showed that longer time was required for froth of smaller bubbles to drain, coalesce, and rupture.

ACTIVITIES FOR NEXT QUARTER

Work on stability of two-phase froth will be continued in the next quarter. Major efforts will be devoted to studies of stability of fine coal froths with respect to:

- half-life time

- drainage time constant

- diffusion time constant

A number of defoaming experiments will also be conducted with coal, magnetite or limestone particles used as defoamer. These particles are to be rendered hydrophobic by coating with surfactants. The parameters to be investigated in these tests include particle size, surfactant concentration and conditioning time, etc.
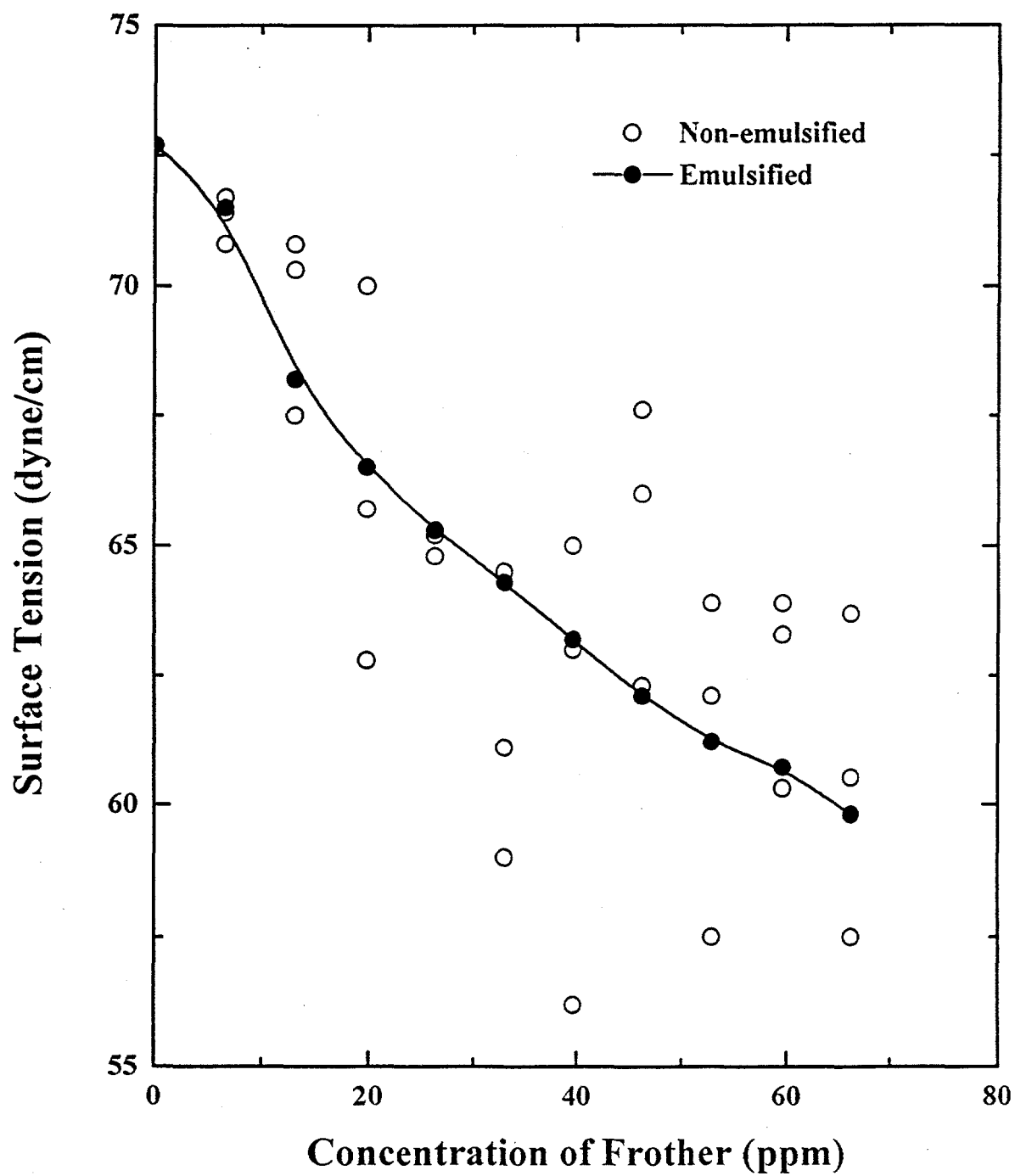
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Figure 1. Change of surface tension with frother concentration up to 66 ppm. The solution was prepared using two different approaches.
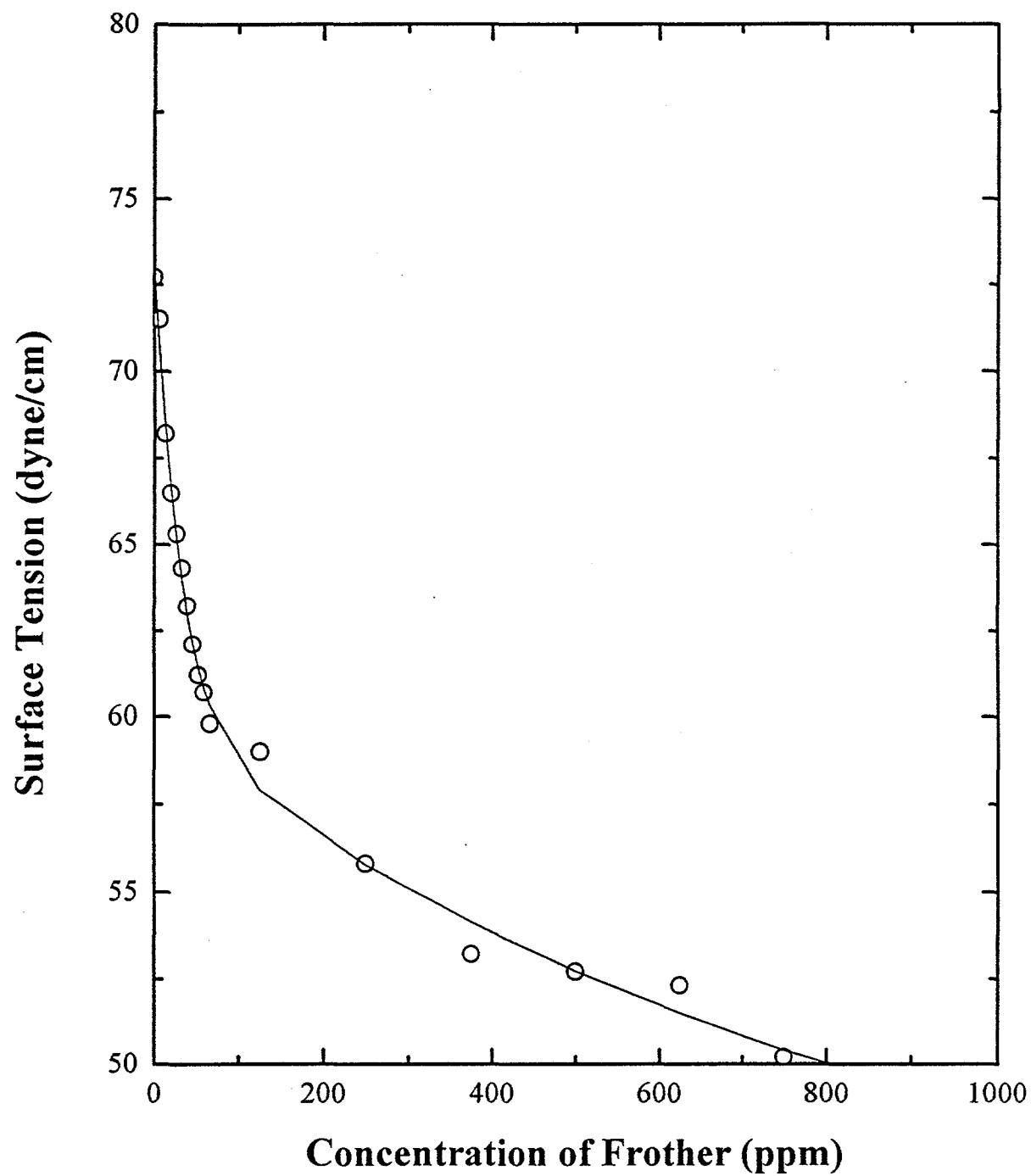
Figure 2. Change of surface tension with the concentration of emulsified frother up to 1000 ppm.
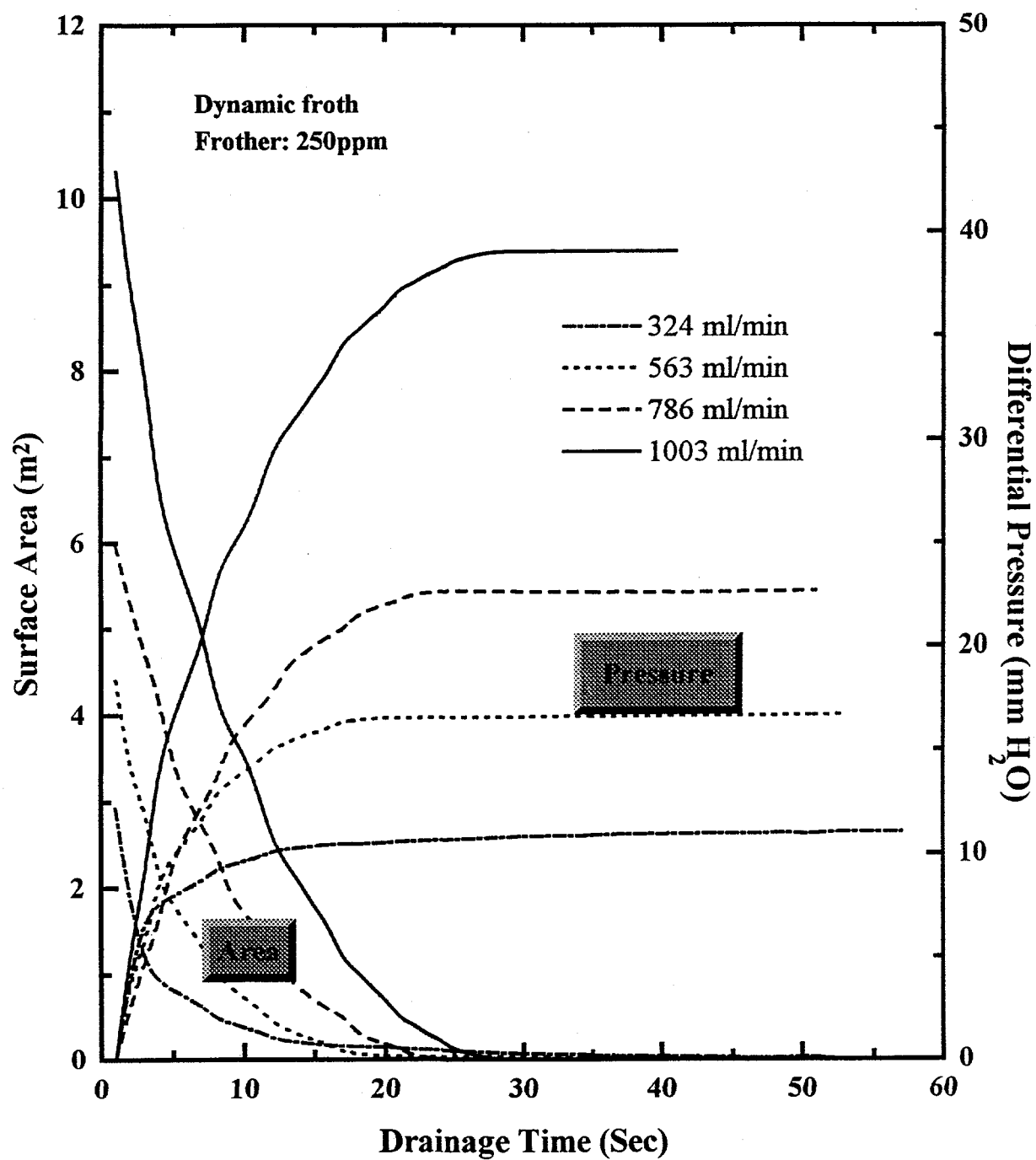
Figure 3.   Differential pressure and surface area obtained with dynamic froth as a function of drainage time using 250 ppm frother concentration.
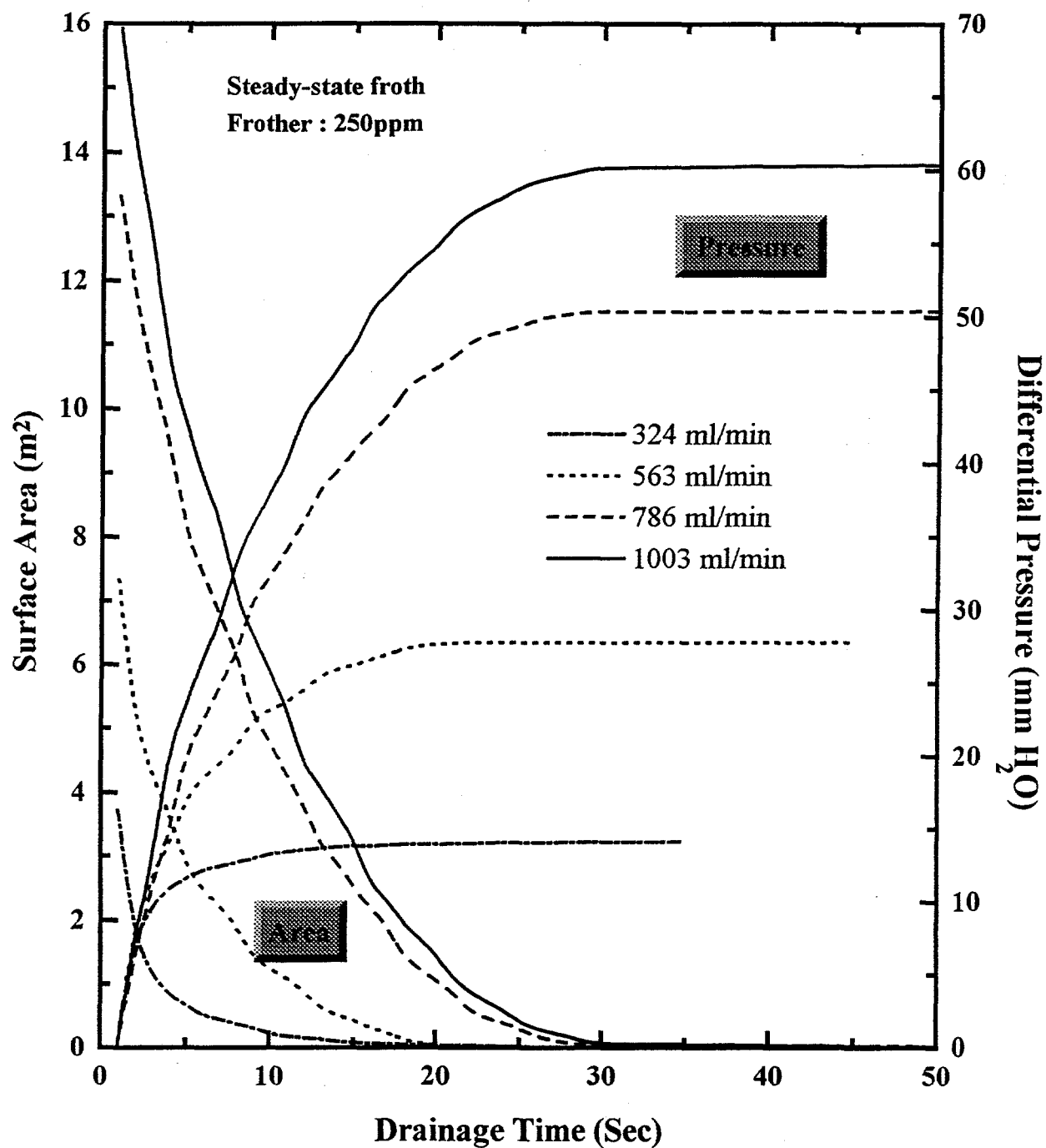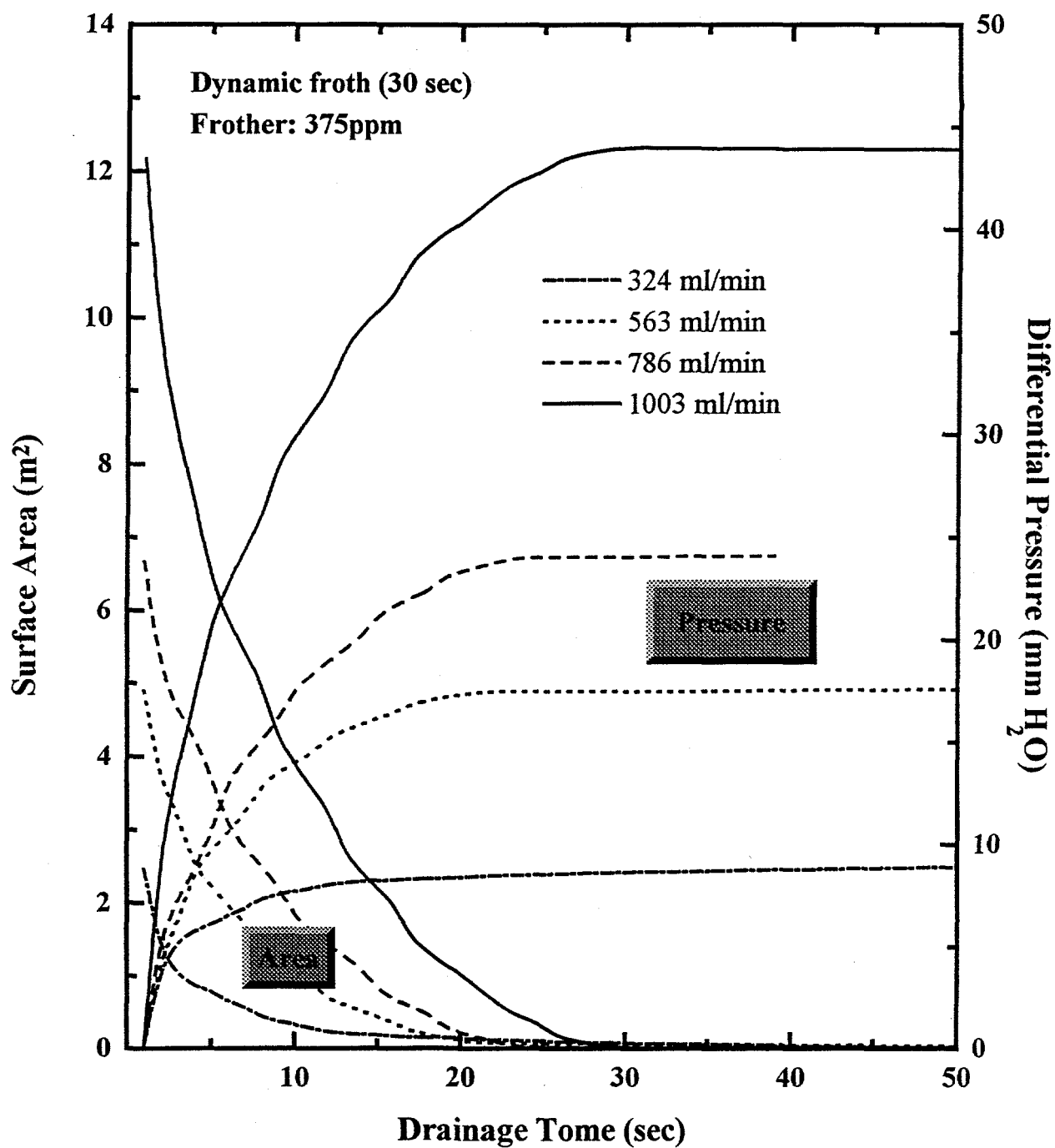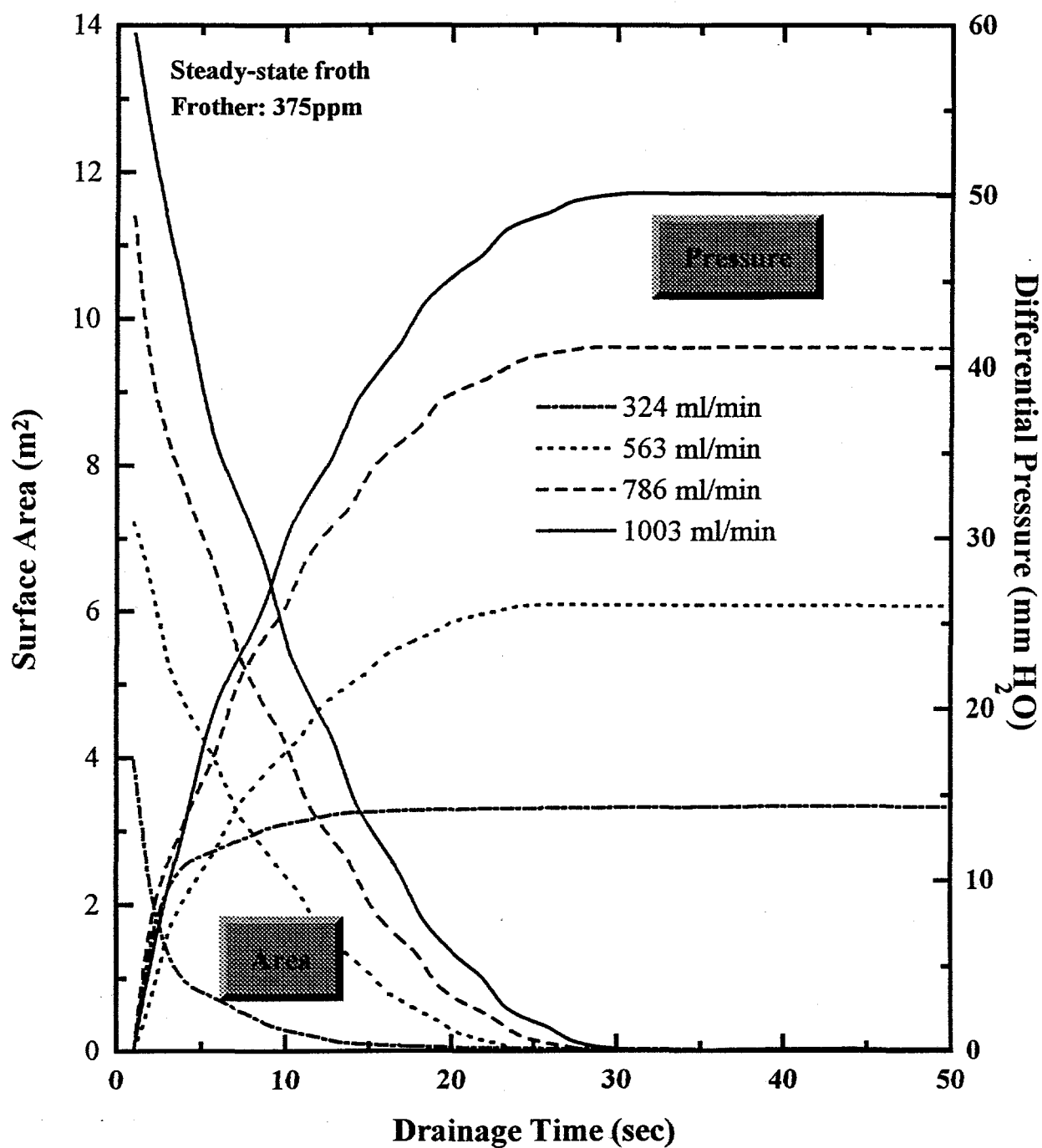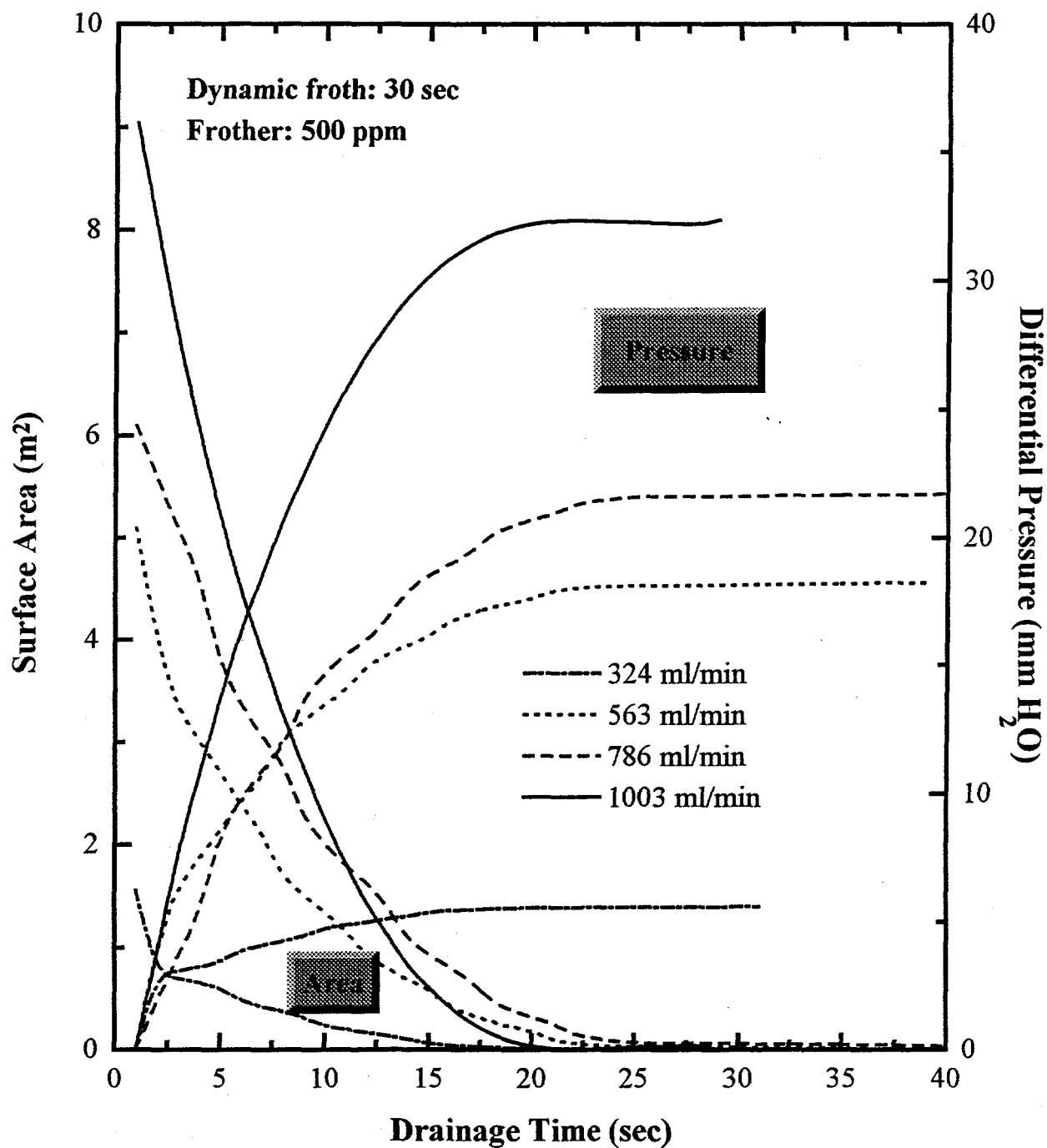
Figure 4.   Differential pressure and surface area obtained with steady state froth as a function of drainage time using 250 ppm frother concentration.

Figure 5.   Differential pressure and surface area obtained with dynamic froth as a function of drainage time using 375 ppm frother concentration.
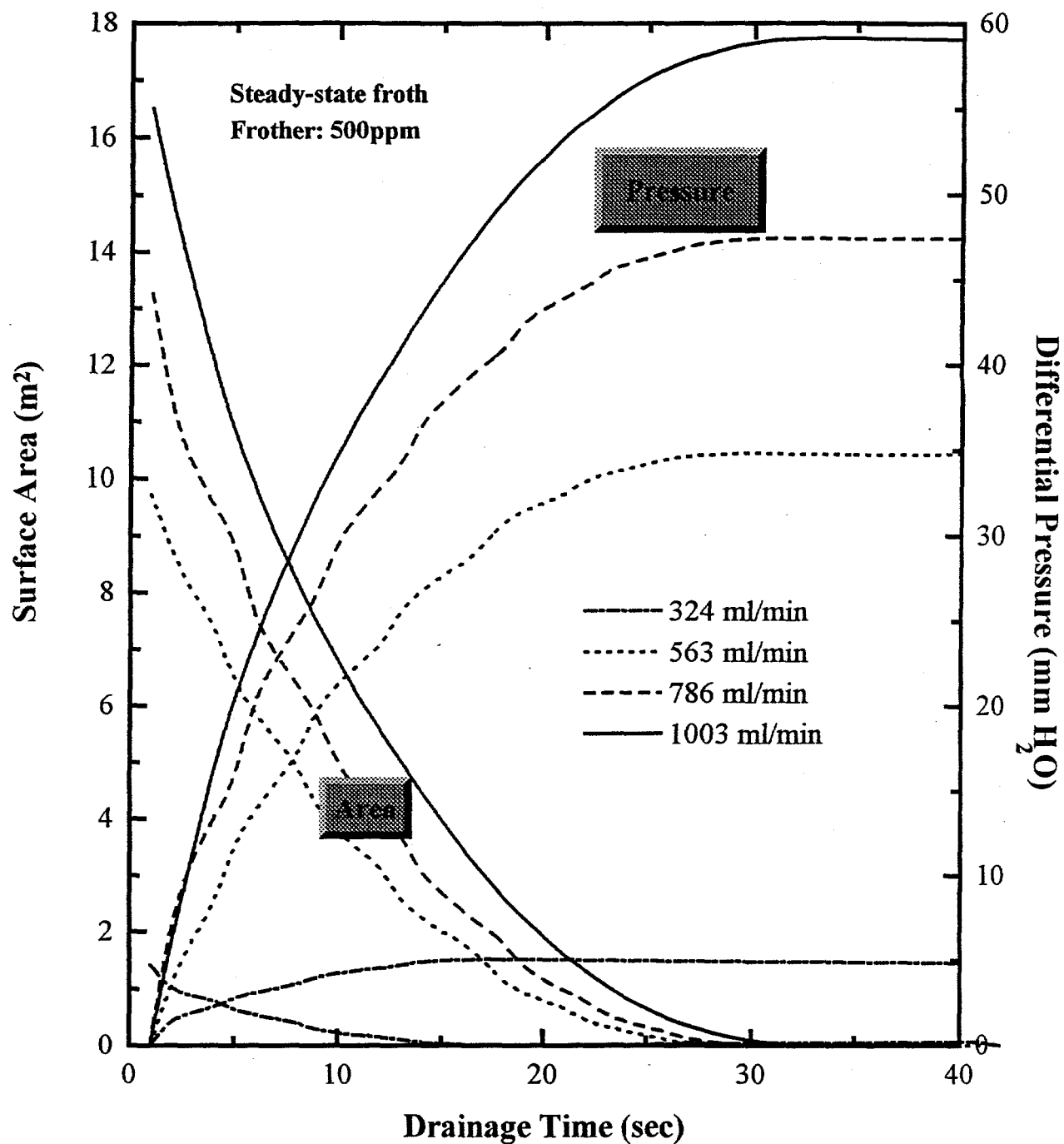
Figure 6. Differential pressure and surface area obtained with steady state froth as a function of drainage time using 375 ppm frother concentration.

Figure 7. Differential pressure and surface area obtained with dynamic froth as a function of drainage time using 500 ppm frother concentration.

Figure 8. Differential pressure and surface area obtained with steady state froth as a function of drainage time using 500 ppm frother concentration.
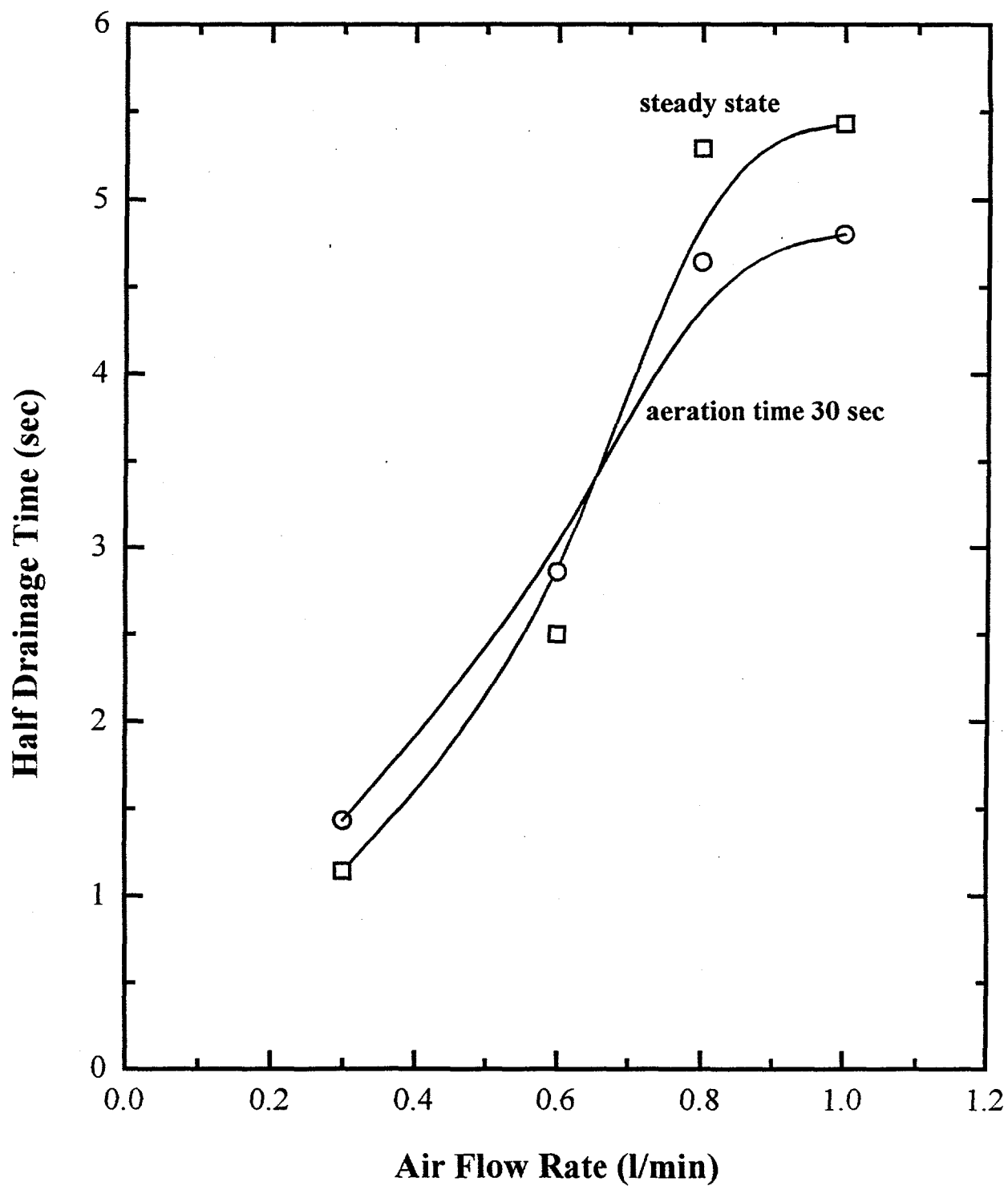
Figure 9.   Half-drainage time vs. air flow rate for dynamic and steady state froth using 250 ppm frother concentration.
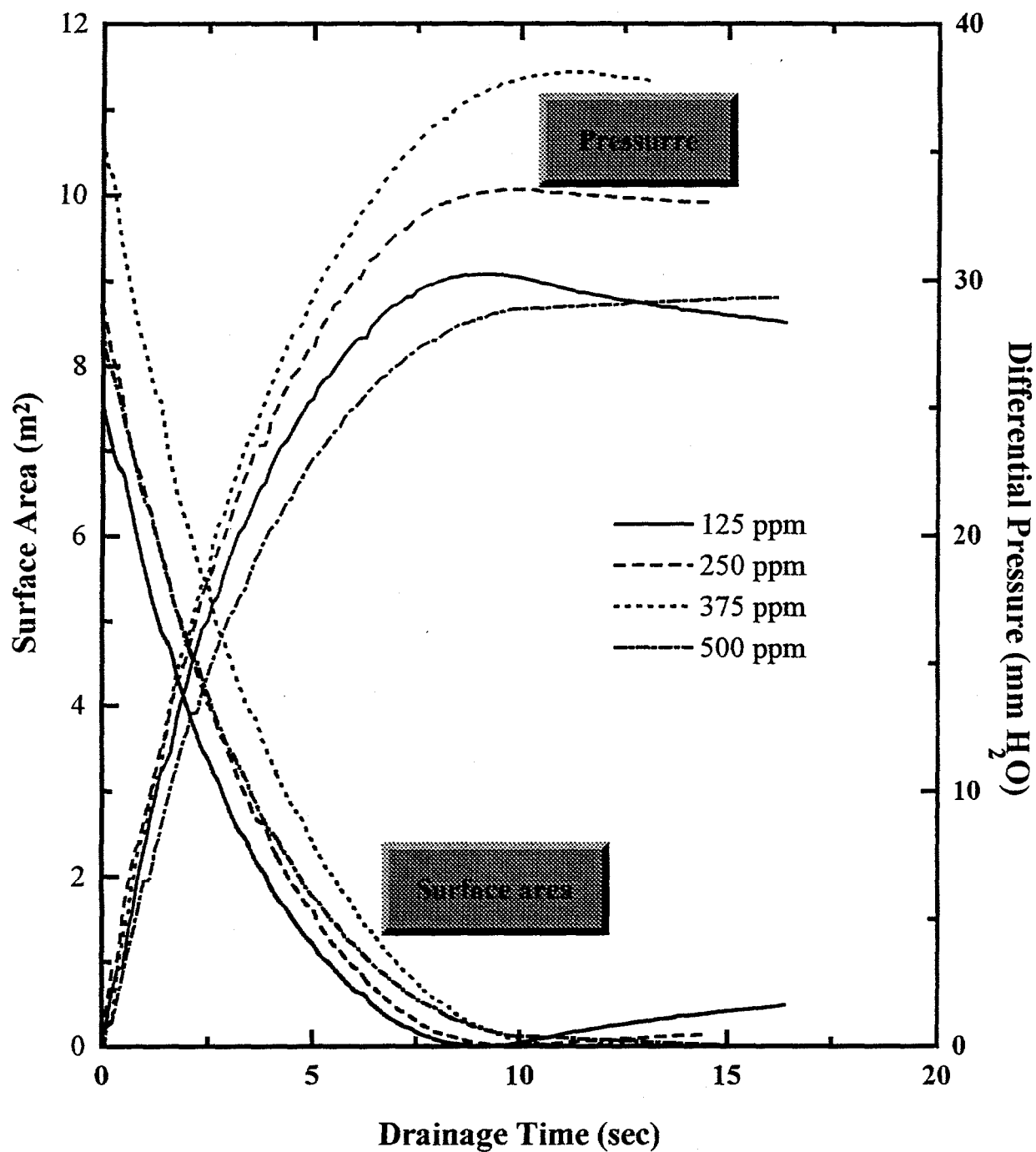
Figure 10. Change of differential pressure and surface area of froth with drainage time at different frother concentrations