



Project Summary

Recovery of Calcium Carbonate and Sulfur from FGD Scrubber Waste

R. P. Arganbright, P. Huang, G. S. Benner, B. G. Mandelik, T. S. Roche, and P. V. Smith

Key process steps were demonstrated in the Kel-S process, a proprietary process for recovering calcium carbonate and sulfur from lime/limestone flue gas desulfurization (FGD) scrubber waste. These steps are reduction of the waste to calcium sulfide (using coal as the reducing agent), carbonation of the calcium sulfide to generate hydrogen sulfide and calcium carbonate, and recovery of precipitated calcium carbonate from inerts (e.g., coal ash).

Conversion of 99 percent of the calcium sulfate/sulfite to calcium sulfide was achieved both in a laboratory furnace and in a pilot plant kiln. Conversion of the sulfide to carbonate and hydrogen sulfide in bench-scale equipment gave very high rates of conversion (less than 1 percent calcium sulfide remaining in the solids), and the concentration of hydrogen sulfide in the offgas typically exceeded 95 percent. Results from flotation, centrifugation, and filtration experiments indicate that all three methods could be used in the ash separation step, but economics favor centrifugation. Technically, the Kel-S process was shown to be ready for testing in a continuous pilot plant.

However, a preliminary economic analysis of the Kel-S process was conducted by the Tennessee Valley Authority (TVA) for EPA. This analysis indicated that the total cost of a limestone scrubbing FGD process using the Kel-S recovery approach was 30 percent higher in capital costs and 19 percent higher in annual revenue requirements than the Wellman-Lord/

Allied Chemical process (which has been demonstrated on a commercial scale by EPA). For this reason, EPA withdrew financial support for the project.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Pullman Kellogg and EPA entered into Contract No. 68-02-2644 which specified that Kellogg would continue research and development of their proprietary Kel-S process under a joint funding arrangement. The process involves a method of converting to usable products the waste produced in lime/limestone flue gas desulfurization (FGD) systems. Major features of the process are production of elemental sulfur using coal as the reducing agent and process fuel and recovery of calcium carbonate for recycling to the FGD system. The following processing steps are involved:

- (1) Reduction of lime/limestone FGD waste (calcium sulfite and sulfate) to calcium sulfide.
- (2) Carbonation of the calcium sulfide to generate hydrogen sulfide and calcium carbonate.
- (3) Separation of inerts (such as coal ash, unreacted coal, limestone inerts, and other impurities) from the calcium carbonate.



- (4) Conversion of hydrogen sulfide to elemental sulfur in a standard Claus plant.

The last step represents well-established commercial technology and was not included as part of this study.

Two distinct inerts-separation process steps were investigated:

- (1) A one-step process which consists of first converting calcium sulfide to calcium carbonate and then removing the inerts from the calcium carbonate by air flotation.
- (2) A two-step process which consists of first converting calcium sulfide to calcium hydrosulfide (which is water soluble) by reaction with hydrogen sulfide, then separating the inerts by filtration or centrifugation, and finally precipitating calcium carbonate from the calcium hydrosulfide solution by reaction with carbon dioxide.

Reduction of the FGD waste occurs in a rotating kiln where the waste and coal are reacted at an elevated temperature to convert calcium sulfite/sulfate compounds to calcium sulfide. The study, as originally planned, consisted of four phases. Phase I included the following tasks:

- (1) Obtain FGD waste feed from a commercial FGD system.
- (2) Dry waste to the level needed for making suitable pellets; determine a suitable pelletizing procedure; determine the coal content needed in the pellets for complete reduction.
- (3) Determine the feed rate for drying the pellets, the kiln operating temperature, and the kiln feed rate.
- (4) Perform a kiln production run to make feed for pilot plant operation.

Phase II involved the following tasks:

- (1) Perform bench-scale carbonation tests to determine the maximum particle size of reduced FGD waste that could be used to obtain suitable carbonation rates, to determine operating conditions needed to obtain maximum concentration of hydrogen sulfide in the reactor off-gas, and to provide information for designing the pilot plant reactors.
- (2) Perform bench scale flotation, centrifugation, and filtration tests to show the feasibility of separating calcium compounds from coal ash and inerts, to determine range of operating conditions for the pilot plant, and to provide information for sizing the pilot plant units.

All of the Phase I and II tasks, except the continuous kiln production run (the fourth task of Phase II), were completed. Phases III and IV involved the design, erection, and operation of a pilot plant for recovery of calcium carbonate (as well as the production of hydrogen sulfide) and separation of coal ash and other inert materials. Most of the design of the pilot plant and delivery of much of the pilot plant equipment was accomplished before the contract was terminated by EPA. (The rationale for contract termination is included in the discussion below.)

Phase I Results

Based on Kellogg in-house data previously obtained in bench scale equipment, pellet compositions were specified for the initial FGD waste reduction kiln test work. Using these compositions, a pelletizing procedure was developed which produced pellets strong enough to be used in rotary kiln operations. The pellets were produced by mixing about 4 wt percent bentonite binder with the dried coal/FGD waste mixture and then spraying a 5 wt percent starch (in water) solution on the pellets as they were formed.

The pelletizing procedure produced pellets of variable quality because spraying the starch solution on the pellets was done manually and was difficult to control in below freezing weather. Several mixtures of materials were tested until it was determined that satisfactory pellets could be produced by pelletizing mixtures containing 2 wt percent bentonite and 2 wt percent wheat starch.

The green (wet) pellets were dried in a pilot flowdryer that kept the pellets agitated above a grate through which hot air (270 °F)* flowed. Attempts to run the dryer continuously were unsuccessful; therefore, batch drying was used. The dried pellets were collected in drums and stored prior to kiln processing.

Using the dried pellets, kiln tests were made in a 24-in. outside diameter, 30-ft long rotary kiln (see Figure 1) at Kennedy Van Saun, Inc. (KVS) in Danville, PA. These tests were conducted to establish the operating conditions necessary to achieve a maximum reduction of the FGD waste. Essentially complete reduction of the calcium sulfate/sulfite compounds to calcium sulfide was achieved (see Table 1).

*Readers more familiar with the metric system are requested to use the conversion table at the end of this summary.

Using a laboratory furnace at the facilities in Houston, TX, Kellogg also conducted reduction tests to expand the data base obtained in the KVS kiln tests. These results confirmed the pilot kiln results and the minimum amount of coal required for complete reduction.

Phase II Results

Using the reduced material produced in the KVS kiln tests, Kellogg carried out bench-scale carbonation tests (see Figure 2) to define operating conditions and produce a feed for the air flotation test to determine whether calcium carbonate could be separated effectively from impurities. The bench-scale carbonation tests indicated that the conversion of calcium sulfide to calcium carbonate and hydrogen sulfide was extremely rapid and apparently limited by the rate at which carbon dioxide could be fed into the system. Maximum concentration of hydrogen sulfide in the effluent gas ranged from 90 to 100 percent for most of the runs (see Table 2), which is ideal feed gas to a Claus plant.

The effect of particle size of the reduced FGD waste was studied using -12 to +140 mesh, and -140 mesh particle-size distributions, but the results were not conclusive. It appears that particle size within the range tested is not critical. The effects of pressure and temperature also were evaluated, but within the range tested (20 psig, 150° to 250°F), no significant differences were observed.

Product produced in the Kellogg bench-scale carbonation tests was used in the air flotation test performed at Denver Equipment facilities in Denver, CO. It was determined that three additives (fuel oil, pine oil, and a proprietary promoter manufactured by American Cyanamid) and three floats were needed to achieve about 75 percent recovery of calcium carbonate and approximately 50 percent inerts rejection. These results indicate that air flotation could be used commercially (see one-step process, Figure 3).

Although air flotation was shown to be technically feasible, the air flotation additives which remained with the recovered ash might preclude the use of the recovered ash as landfill because of waste disposal environmental regulations. Significant amounts of calcium carbonate (25 percent) would also be rejected with the ash. It was then decided to examine the use of filtration and centrifugation to remove ash from the system.

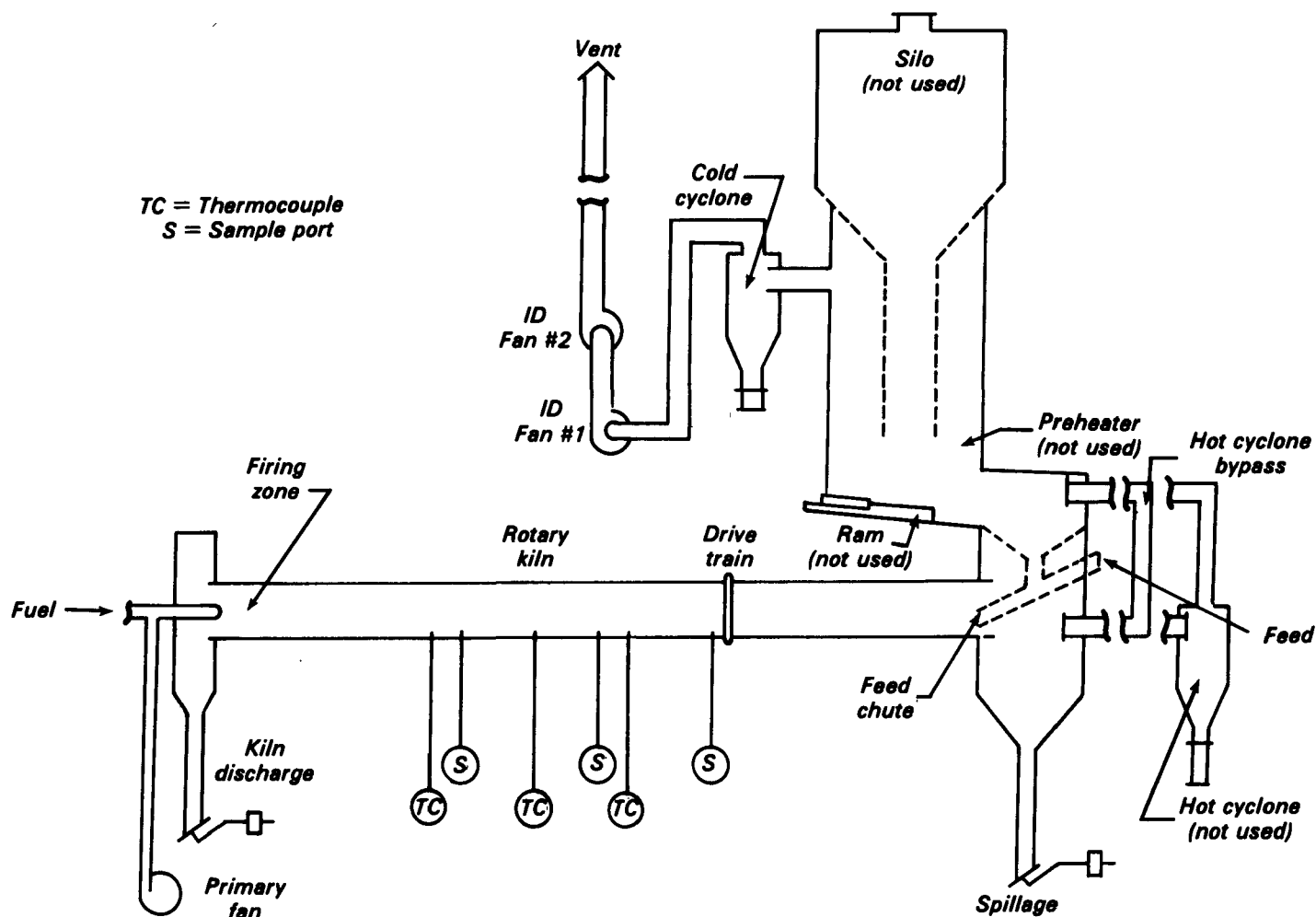


Figure 1. Kennedy Van Saun (KVS) rotary pilot kiln.

Table 1. Kel-S Pilot Plant Analyses—Mixture K1 Kiln Test (November 21-22, 1977)

Sample Description	Time Sample Taken	Date Sample Taken	CaS, wt %	CaSO ₃ , wt %	CaSO ₄ , wt %	CaCO ₃ , wt %	CaO, wt %	Al ₂ O ₃ , wt %	FeO, wt %	MgO, wt %	Free Carbon, wt %
KD*	2 p.m.	11/21/77	41.07	3.23	0.46	0.89	26.49	2.70	2.74	0.93	2.66
Port 1	2 p.m.	11/21/77	38.56	0.60	0.61	3.65	23.67	2.88	2.63	0.75	7.80
KD	4 p.m.	11/21/77	38.38	1.35	0.20	0.0	25.51	2.00	1.83	0.67	1.49
Port 1	4 p.m.	11/21/77	40.05	0.0	0.21	3.06	23.10	2.64	2.51	0.79	9.92
Port 3	4 p.m.	11/21/77	1.30	0.15	39.15	21.15	4.60	0.51	0.89	0.30	—
KD	6 p.m.	11/21/77	42.83	0.30	0.48	0.28	23.25	2.44	2.08	0.72	1.64
Port 1	6 p.m.	11/21/77	38.10	0.15	0.59	4.68	23.72	2.60	2.26	0.69	10.29
KD	11 a.m.	11/22/77	41.07	0.0	0.85	0.69	26.74	2.92	2.53	0.79	4.32
Port 1	11 a.m.	11/22/77	6.40	0.0	32.87	20.67	8.63	1.31	1.61	0.44	12.43
KD	2 p.m.	11/22/77	42.59	0.30	0.0	0.57	25.72	3.20	2.89	0.84	5.27
Port 1	2 p.m.	11/22/77	18.45	0.0	15.48	20.94	10.32	1.94	1.81	0.58	11.67
KD	4 p.m.	11/22/77	43.48	0.0	0.72	1.06	22.45	2.86	2.53	0.82	4.21
Port 1	4 p.m.	11/22/77	25.77	0.0	13.84	18.91	8.41	1.95	1.76	0.58	10.64
Port 3	4 p.m.	11/22/77	1.21	0.0	39.57	19.15	4.43	0.44	0.73	0.32	—
KD	6 p.m.	11/22/77	37.91	0.30	0.51	2.18	24.86	2.68	2.27	0.77	7.66
Port 1	6 p.m.	11/22/77	21.88	0.0	11.93	17.07	12.13	1.86	1.59	0.58	12.71

*Kiln discharge.

Table 2. Carbonation Test Results

Run No.	FGD Waste Slurry		Reactor Conditions		CO ₂ Feed Rate, /min	Maximum H ₂ S Concentration, %
	Percent Solids	Total Volume,	Temp, °F	Press., psig		
1	15	2	260	60	1.0	74.5
2	7.3	2	250	60	1.0	46.4
3	25	2.4	250	60	1.0	55.9
4	15	2	250	60	0.54	57.5
5	15	2	250	60	0.54	15.6
6	7.3	3	250	60	0.54	81.5
7	7.3	3	250	60	0.54	44.4
8	7.3	2	250	60	0.54	61.3
9	7.3	3	250	60	0.54	44.5
10	7.3	3	250	60	1.0	39
11	7.3	3	250	60	0.54	96.9
12	7.3	3	250	60	1.0	93.9
13	7.3	3	250	60	0.54	97.8
14	7.3	3	250	60	1.0	88.6
15	7.3	3	250	60	1.5	83.8
16	7.3	2	250	60	1.0	92.1
17	7.3	3	250	60	1.0	88.7
18	7.3	3	275	74	1.5	83.8
19	7.3	3	250	60	1.0	90.7
20	7.3	3	250	60	1.5	97.9
21	7.3	3	200	42	1.5	97.9
22	7.3	3	200	42	1.5	98.2
23	7.3	3	250	60	1.5	—
24	7.3	3	150	35	1.5	96.8
25	7.3	3	200	42	1.5	97.4
26	7.3	3	200	24	1.5	93.9
27	7.3	3	250	60	1.5	98.1
28	7.3	3	250	60	1.5	99.3

The two-step process consists of (see Figure 3):

- (1) Dissolving calcium sulfide by adding hydrogen sulfide, thus forming soluble calcium hydrosulfide.
- (2) Removing the insoluble ash by filtering or centrifuging.
- (3) Precipitating the calcium as calcium carbonate from solution by adding carbon dioxide.

Kellogg conducted several bench-scale semi-batch (i.e., continuous gas flow, batch liquid/solids) tests which demonstrated the calcium dissolution and calcium carbonation steps. The maximum percent hydrogen sulfide generated in the carbonation step ranged from 86-98 percent hydrogen sulfide, which is ideal for sulfur plant feed. The precipitated calcium carbonate was extremely pure (99.37 percent), and should be excellent recycle to a limestone scrubbing unit.

The two-step intermediate product (ash and dissolved calcium/sulfur values) was sent to the Bird Machine Company, South Walpole, MA, for centrifuge and filter tests. Both tests indicated better calcium recovery and less calcium rejection than the results in the air flotation tests.

Economic Analyses

Using the data from these tests, Kellogg did a process evaluation to compare the relative costs of solids removal equipment for the one- and two-step processes (see Table 3). Although the air flotation units have the lowest capital cost, the penalties of lower separation efficiency and potentially polluting additives made air flotation less attractive than filters or centrifuges. For this application, centrifuges were preferable (over filters) because of lower capital costs. As a result of the evaluation, the pilot plant design was changed to use the two-step process and to incorporate a centrifuge as the ash separation device.

Although the results of the study indicated that the process was technically feasible, unforeseen problems early in the study led to delays and additional expense, resulting in a large projected cost overrun under the contract. To assist in the decision of whether to continue the study, EPA requested the Tennessee Valley Authority (TVA) to conduct a preliminary economic evaluation of the Kel-S process. TVA based the evaluation on design and economic premises developed jointly by EPA and TVA to evaluate a variety of FGD processes. Some of the

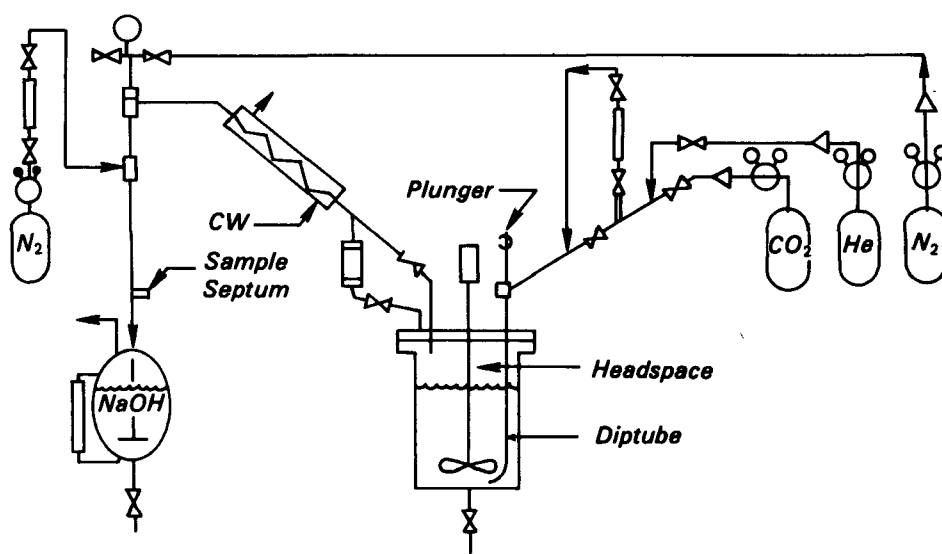


Figure 2. Kel-S carbonation bench-scale unit.

Table 3. Cost Comparison of Air Flotation Versus Centrifugation/Filtration for the Kel-S Process

Method	Approximate Capital Cost, \$1000	Percent Feed CaCO ₃ Recovered	Percent Feed Ash Rejected	Raw Material Costs			Notes
				Makeup CaCO ₃ , \$1000/yr	Additives, \$1000/yr	Total, \$1000/yr	
One-Step							
Air Flotation (Using results from Denver Equipment Experiment 17)	65	76	52	414	307	721	Additives: Pine Oil, Fuel Oil, Aeropromoter 845
Air Flotation (Using results from Denver Equipment Experiment 9)	110	74	62	455	643	1098	Additives: Aeropromoter 839 and 845, Accoalfroth S-4005
Two-Step							
Centrifuge	200	77	92	402	0	402	
Centrifuge (washed)	400	86	84	243	0	243	Cake reslurried and recentrifuged
Centrifuge	200	74	97	455	33	488	Additive: Percol 725 0.2 lb/t
Centrifuge (washed)	400	83	93	288	33	321	Additive: Percol 725 0.2 lb/t, cake reslurried and recentrifuged
Filter	900	79	100	363	0	363	
Filter (washed)	900	90	100	172	0	172	Cake washed on filter

main premises were (1) the FGD system was to be installed on a new 500-MW boiler burning 3.5 percent sulfur, 16 percent ash coal; (2) the FGD system was designed to control SO₂ emissions to 1.2 lb/10⁶ Btu heat input; (3) capital costs were projected to mid-1979, representing a mid-1977 construction start and a mid-1980 completion; and (4) annual revenue requirements (operating costs + capital charges) were based on a 7000 hr/yr first year operation and were projected to mid-1980. Results of the evaluation are summarized in Table 4.

The TVA evaluation indicated that a limestone scrubbing Kel-S process was almost 50 percent higher in capital costs than a typical limestone scrubbing process with ponding of the waste; the Kel-S annual revenue requirements were about 80 percent higher than ponding the waste. When compared to the Wellman-Lord/Allied Chemical process, which also produces elemental sulfur, the Kel-S process fared somewhat better, but not enough to make it competi-

Table 4. Comparative Costs of Kel-S Versus Competing FGD Processes

Costs, \$1000	FGD Processes		
	Limestone FGD + Ponding	Limestone FGD + Kel-S	Wellman-Lord/ Allied Chemical
Total Capital Investment	48,728	73,023	56,295
Total Annual Revenue Requirements	14,102	26,065 ^a	21,982

^aBy-product sulfur sales credit excluded; at \$60/long ton, this would be about \$2 million/yr.

tive (see Table 4). For this reason, EPA withdrew financial support from the contract.

Conclusions

All steps in Phases I and II, except the kiln run to produce feed material for the pilot plant, were completed. The FGD waste sludge was reduced satisfactorily in all three kiln test runs.

Carbonation tests conducted with the bench scale reactor show that the rate of conversion of calcium sulfide to calcium carbonate and hydrogen sulfide is rapid, and that high purity levels of hydrogen sulfide in the effluent gas are achievable.

Flotation, filtration, and centrifugation experiments, environment considerations, and analysis of equipment costs indicated that the two-step Kel-S process using centrifugation was preferable.

The objectives of Phases I and II were successfully demonstrated. On this basis, it would have been technically sound to proceed with erection and testing of the pilot plant. However, an economic evaluation of the Kel-S process indicated that it probably could not compete with other FGD processes.

Metric Conversion Factors

To Convert from:	To:	Multiply by:
Btu	J	1,055.1
°F	°C	$\frac{5}{9}(\text{°F} - 32)$
ft	cm	30.48
gal	l	3.785
in.	cm	2.54
lb	kg	0.454
psig	kP	6.895

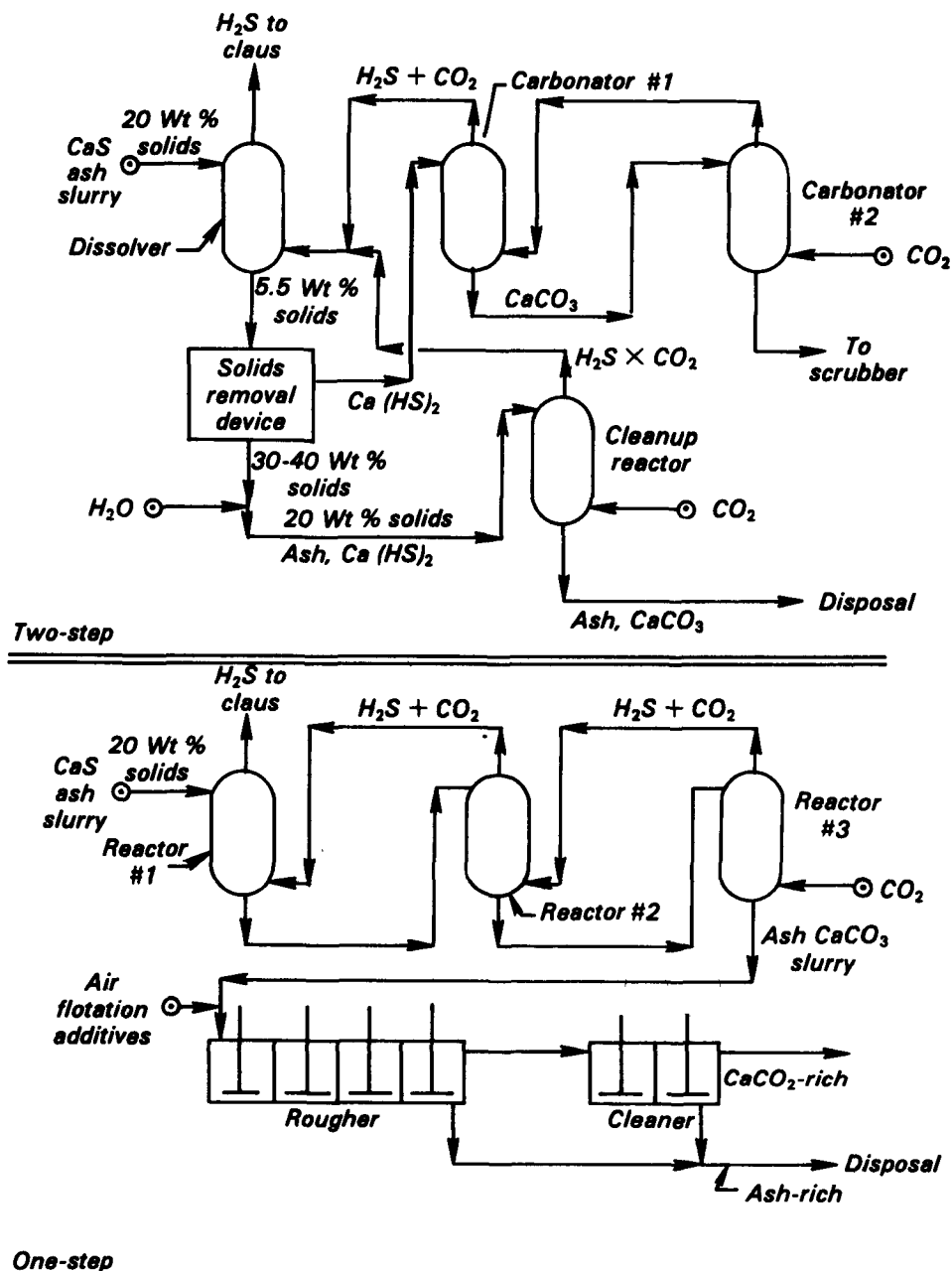


Figure 3. Process comparison, one- and two-step processes.

R. P. Arganbright, P. Huang, G. S. Benner, B. G. Mandelik, T. S. Roche, and P. V. Smith are with Pullman Kellogg, Industrial Park Ten, Houston, TX 77084.

Julian W. Jones is the EPA Project Officer (see below).

The complete report, entitled "Recovery of Calcium Carbonate and Sulfur from FGD Scrubber Waste," (Order No. PB 82-227 729; Cost: \$13.50, subject to change) will be available only from:

National Technical Information Service

5285 Port Royal Road

Springfield, VA 22161

Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

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