MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES

3 4456 0263774 2

ORNL/TM-10471

ornl

OAK RIDGE
NATIONAL
LABORATORY

MARTIN MARIETTA

Catalytic Sodium Hypochlorite Degradation Using a Kynar Stabilized Catalyst

A. L. Compere
W. L. Griffith

OAK RIDGE NATIONAL LABORATORY
CENTRAL RESEARCH LIBRARY
CIRCULATION SECTION
4500N ROOM 175
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this report, send in name with report and the library will arrange a loan.

OPERATED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
NTIS price codes—Printed Copy: A03; Microfiche A01

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ORNL/TM-10471

Catalytic Sodium Hypochlorite Degradation Using a Kynar Stabilized Catalyst

A. L. Compere
W. L. Griffith

Date Published: June 1987

Prepared by the Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831
operated by
Martin Marietta Energy Systems, Inc.
for the
U. S. Department of Energy
under Contract No. DE-AC05-84OR21400

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES

3 4456 0263774 2

Contents

Abstract v

1. Introduction 1
   Historic Overview 1

2. Experimental Plan 4

3. Results 6

4. Discussion and Recommendations 13

5. Process Implications 17

6. Materials and Methods 18
   Catalyst Columns 18
   Column Feedstock 18

7. References 20

Abstract

The efficiency of a patented Kynar-cobalt catalyst manufactured by Harshaw-Filtrol under license agreement with Pennwalt in decomposing waste hypochlorite has been assessed using several alternative process arrangements. Based on bench scale data, it appears that the Kynar-cobalt oxide catalyst developed by Pennwalt is able to treat waste hypochlorite streams. The effectiveness of the catalyst rises as a function of decreasing pH and increasing temperature. For discharge, hypochlorite concentrations on the order of 1 mg/liter are necessary. At temperatures of 55 to 70 C, it is possible to meet these requirements using a single pass through an upflow 40 cm (16 in.) deep catalyst bed. No other input chemicals are required. Solution pH will be reduced somewhat, due to the buffering action of NaCl at high pH. The size of a Pennwalt unit for a given flow/concentration can be estimated based on a simple model. The discharage requirement can also be met by other configurations, including two-stage columns connected in series and downflow units, with roughly the same amount of catalyst for a given temperature and concentration regime. Based on bench experience, construction and operation of a full scale unit appears economically feasible. Operating problems with the system include attrition, catalyst conditioning and storage. Catalyst attrition is a major problem. Pennwalt itself required reformulation of the catalyst in order to decrease attrition during scale up from laboratory to pilot use. In our bench tests, catalyst loss from a tared laboratory column across several weeks was about 0.5 gram per gallon of concentrated hypochlorite processed or, using current Pennwalt costs of $50/lb catalyst, $55 per 1,000 gal. Attrition is thought to result from explosion of the catalyst by oxygen gas trapped in internal pores of the catalyst. Several operating parameters can increase the rate of catalyst breakdown: high hypochlorite concentrations, increased temperature, and decreased pH. Once attrition begins, increased catalyst movement (decreased catalyst in the column) increases breakdown due to mechanical abrasion. Operations methods can be planned to decrease catalyst breakup by limiting the rate of hypochlorite degradation. These could include lowering the concentration of hypochlorite in the feedstock and operating under conditions in which the catalyst produces less oxygen per volume of catalyst. Alternatively, a lower efficiency catalyst could be formulated, using more Kynar and less cobalt oxide, by Harshaw-Filtrol. However, easy catalyst reloading should be part of any equipment design. During first use, a gradual increase in hypochlorite concentrations for several hours appears necessary. In re-uses of the bed after storage, at least a half hour of use is required for consistent minimal hypochlorite output. During startup periods, provision for effluent recycle is recommended. Wet storage of catalyst is recommended by previous investigators since drying may cause loss of activity.

1. Introduction

The removal of hypochlorite from industrial alkali streams has been a process challenge for many years. These streams are produced by electrolytic production of chlorine and from the removal of chlorine by caustic scrubbing. Depending on industrial process constraints, hypochlorite concentrations can range from less than 1% to above 10%. Although hypochlorite can be used as an industrial germicide, a chlorinating agent for environmental control processes, and a bleaching agent, the presence of other stream constituents can limit its use. Where this is the case, methods which convert waste hypochlorite to chloride can be used to facilitate disposal or chloride recycle. Oxygen gas, a byproduct of some conversion processes, can be readily discharged.

Historic Overview

Reactions producing oxygen from hypochlorite in the presence of metallic oxides were reported as early as 1834 by Ballard and confirmed by other investigators (Gay Lussac 1842, Mitscherlich 1843, and Bidet 1886). Early studies were directed towards the production of oxygen gas from hypochlorite in the presence of oxides of silver, cobalt, nickel, copper, iron, and barium. Later, investigations of the degradation of industrial hypochlorite in containing or in contact with metals were also reported (Muspratt and Smith 1898, Gerland 1891, White 1903, and Hoffman and Ritter 1914). Although these studies involved hypochlorite degradation, they were primarily focussed on prevention, rather than kinetics.

After World War I, there was increased interest in the investigation of the kinetics of catalytic processes. To indicate the types and utility of studies performed during this period, a few are summarized in detail. The mediated degradation of hypochorite with the release of oxygen was reported in 1923 by Kind. His work was followed by Howell's reports on the decomposition of hypochlorite by cobalt peroxide (1923). Howell prepared and crystallized the cobalt peroxide, washing it several times to remove residual alkali. He introduced the cobalt oxide as a few percent of the volume of a solution containing 1.14 *M* each of NaOCl and NaCl, 0.28 *M* NaOH, and 0.16 *N* Na_2CO_3. Effect of variation in process parameters including temperature, NaCl, and NaOH was studied. The Arrhenius temperature coefficient derived was 2.37 to give an activation energy of 16,574 cal. The author also reported that the addition of NaCl increased the rate of reaction, while decreasing alkali increased the rate of reaction.

Lewis (1928) studied the decomposition of alkaline hypochlorite solutions with copper, ferric, and cobalt sulfates, cobalt peroxide, and copper and iron oxides. Continuous measurements of gas evolution were made until reaction ceased except in the case of continuous flow systems. He noted investigated several features of interest in current and conventional systems: the promoter effect shown by mixed copper and iron oxides and the marked effect of temperature on catalytic systems containing cobalt sulfate (cobalt ions) or oxide (solid). The promoter effect has been shown by many investigators since, and indicates that, for some metal combinations, a composition of can be found where a two metal mixture performs better then either metal alone. Lewis reported an Arrhenius coefficient of 2.02, slightly less than that reported by Howell, for cobalt oxide. However, he indicates that the reaction rate is essentially a function of catalyst,

rather than hypochlorite, concentration: a zero order reaction, as long as hypochlorite is in excess.

Since that period, a number of authors have reported catalysis of of hypochlorite degradation by a variety of transition metal oxides and hydroxides (Gray and coworkers 1977, Hamano and coworkers 1977 and 1985, Mori and Hamano 1984). Other authors have studied the hypochlorite decomposition by soluble salts such as metal chlorides (Krunchak 1974). In their investigation of the effect of soluble salts of cobalt, nickel, and iron on hypochlorite degradation, Patel and Mankad (1954) concluded that cobalt sulfate and ferric ammonium citrate show the highest acceleration of rate.

Attachment of the catalyst to a permanent substrate which prevents its release from the treatment system without unduly decreasing its effect has been a major concern in practical systems. Kurlyandskaya *et al* investigated the decomposition of hypochlorite solution using copper, nickel, or iron hydroxides entrained in silica or alumina gels (1972). This development resulted in the issuance of a Russian patent. Caldwell and coworkers developed practical methods for the decomposition of hypochlorite using cobalt oxide spinels deposited on a common chemical process substrates (1978, 1983). This trend has been continued to cover varied catalyst supports, including aluminum gels (Kurlyandskaya *et al* 1972), plexiglass (Denisoys and Agaltsov 1970), vinyl chloride (*ibid*), zeolites (Kinosz 1976), milk of lime (Makarov and Shreibmann 1956), aluminum silicates (Caldwell and Fuchs 1978), chemical stoneware (*ibid*), alumina (*ibid*), titanium sponge (*ibid*), and Kynar (Pennwalt 1981, Clark and coworkers 1980 and 1983). Preference varies with investigator. Some investigators have simply used the catalyst as fused metal or salts. Other inestigators have successfully used metal activated carbons as catalysts (Tarkovskaya *et al* 1979 and Mitsubishi 1981). The processes admit considerable variation in technique, while still giving reasonably consistant results. Some authors even report integration of a hypochlorite degradation system into the alkali scrubbing operations typically used to remove chlorine gas as hypochlorite (Gokhale and Frank 1982).

Reports on the effect of mixed systems vary considerably, with some authors indicating a synergistic effect, and other indicating that the major effect could be obtained with mixtures of two metal oxides or hydroxides. In some cases, a particularly fortuitous combination, such as the bimetallic spinel catalyst patented by Crawford and Wadsworth (1981) can be selected. In general, the major effect of combined metal oxides is simply an increased effective pH or temperature zone. In support of this contention, the activation energies reported by many investigators are reasonably constant, generally on the order of 14 to 16 kcal/mole for many catalyzed systems. Various mathematical treatments of the catalytic process itself have been developed (Ciurlizza and Mojica 1983).

Decomposition using a fixed catalyst has the advantages of a relatively low materials cost coupled with reasonable simplicity of operation. However, from a fundamental process engineering standpoint, the several process design constraints appear to be difficult to meet for the concentrated solutions characteristic of current in-house streams.

The catalytic hypocholorite degradation process has two major physical-chemical constraints. The decomposition of hypochlorite is a fairly exothermic process. The standard state enthalpy of formation change for the decomposition of aqueous NaOCl is 14.6 kcal per gram mole at 25°C. This, corrected for activity coefficient, gives a about 14°C liquid temperature increase resulting from conversion of a 10% NaOCl solution to NaCl.

Additional process heat can be an advantage in terms of increased reaction rate, but a disadvantage in terms of mixing and precise process control. Oxygen, the gaseous process product, is a rapidly evolved and relatively insoluble gas. This causes a substantial increase in expected mixing, decreasing the amount of hypochlorite removed versus that expected in a more ideally plug-flow situation. Additionally, oxygen is evolved at liquid-catalyst contact points, including those within the catalyst itself. At high process loading rates, catalyst particles can be literally blown apart by oxygen. This has caused Pennwalt to produce a second generation catalyst with a lower concentration of cobalt oxide and, hopefully, a longer process lifetime. However, the easy replacement of catalyst in any industrial system is a major design requirement, since it will typically have to be done at least annually. Pivovar and coworkers reported treatment of excessive foam using a chemical antifoam (1979).

Catalyst effectiveness is also affected by pH and temperature. At pH values below 8.5, cobalt is leached from the catalyst. As pH increases above 9, the effectiveness of the catalyst significantly decreases, and expected pH values of a given system are a major process design constraint. As would normally be expected for a catalytic reaction, rate increases roughly exponentially with increasing temperature.

Many authors have reported a decrease in the catalyst effect with time and reuse. However, for the types of systems used industrially, the results reported by Londhe and Kamath (1975), showing a relatively slow, but discernable, decrease in activity or effect, appear more typical. It is difficult, based on these papers, to determine whether the loss of effect is due to catalyst blinding, metal oxide loss from the system, or simple dilution of the effective oxide with less effective precipitates.

2. Experimental Plan

The complexity of the catalyst systems reported by various investigators, together with the catalyst redesign required by Pennwalt to transition between bench scale experimental work and industrial process streams indicated a need for experimental evaluation of their catalyst. The relatively high cost of the Kynar-cobalt oxide catalyst, usually around $50/lb, also provided incentive for process optimization. However, the major reason for investigating the behavior of the Pennwalt catalyst was supplied by the manufacturer: rapid degradation of the early "research grade" catalyst in operation on process streams. The concentration differential which forced reformulation of the Pennwalt catalyst was very small compared to the differential between Pennwalt and Oak Ridge process stream concentrations. This small differential – about 1% – caused a reasonably complete physical breakup in their catalyst within a few week period. The differential under consideration was on the order of 5 to 8%. Neither the literature, which is primarily devoted to stirred reactors, nor Pennwalt could provide data covering our expected operating range, in terms of concentration, pH, temperature, contaminants, and column flow arrangements.

In order to provide a basis for design, several types of basic information on the Pennwalt catalyst were needed: the effect of pH, Cl content, NaOH concentration, temperature, and operating time. These parameters were indicated to have a significant effect on the performance of the catalyst. Jacketed columns with 1 in. diameter by 16 in. long catalyst beds were used. These columns provided an internal diameter at least 10 times average catalyst particle size, as detailed later in *Materials and Methods*. Overall retention times of several minutes were used.

Per the manufacturer's instructions, the catalyst bed was supported on small glass packing and topped with more small glass packing. This arrangement permitted testing of upflow and downflow column operation, recirculation to a stirred reservoir, and series operation of two columns. Weight of air dried catalyst before and after several weeks of operation gave a rough measure of the amount of catalyst attrition during sustained operation.

A range of temperature, concentration, and pH spanning the range of conditions reported by Pennwalt and possible in an Oak Ridge installation was covered. Temperatures from 25 to 70°C were investigated. Hypochlorite concentrations, reported as Cl, fell between 7 and 10 grams per liter. Feed pH ranged between 9.8 and 13.5. Feed rates ranged from below 0.02 ml/s to nearly 1 ml/s.

Design and operating parameters were obtained by direct volumetric and gravimetric measurement of fluid flow to and from the columns, coupled with hypochlorite, pH, and alkalinity measurements using Y–12 Analytical Laboratory's standard techniques. In general, the approach was to test gradually increasing concentrations of simulated and real process stream material at standardized flow and temperature conditions using a variety of alteranative process flow schemes. Several alternatives were tested in the hopes of mitigating probable effects of the high rate of gas evolution during hypochlorite conversion, since this was thought to be responsible for short circuiting the process as well as breaking the catalyst up.

Because of the complexity of the kinetics involved, the mathematical model used to correlate the results was based on the simplistic model used by Pennwalt for packed-bed systems. The first model included only temperature and pH as independent variables in order to be consistant with Pennwalt. In a second model additional variables were added to cover the wider feed con-

centration range. Here in addition to temperature and pH, feed Cl concentration and flowrate were also included because previous investigators had found that the kinetics were not necessarily first order over a wide concentration range. Also oxygen evolution (mixing) should increase in the packed-bed with both flowrate and ClO^- feed concentration.

3. Results

Small 2.5cm diameter by 40 cm long (1×16 in.) columns filled with the Pennwalt Kynar-cobalt oxide catalyst were operated at temperatures between 25°C and 70°C, across a wide range of hypochlorite concentrations, feed rates, and excess NaOH. Concentration, feed, and temperature ranges were extended beyond those investigated by Pennwalt in order to better reflect waste treatment applications. As shown in Table 3.1, it was possible to obtain reasonable hypochlorite conversion at 25°C with adjustment of feed pH to 9.8. Flow rates were in a reasonable design and operating range. It should be noted that the rates obtained, however, were significantly less than those obtained by Pennwalt, at the low pH values used in early bench-scale results presented by Gardner (1980). It is also noteworthy that the catalyst currently supplied by Pennwalt has a higher Kynar content than the early catalyst and should be expected to be less active. For the higher pH runs, no Pennwalt data for comparison was available.

Table 3.1. Upflow runs at 25°C using Pennwalt catalyst

Feed Cl, mg/l	Feed Rate, ml/s	Effluent Cl mg/l	Feed pH	Fraction Cl Removed	Measured Reaction Rate s^{-1}	Run No.
8,333	0.0178	9	12.8	0.99894	0.00061	3
8,510	0.0258	71	12.7	0.99167	0.00062	2
	0.0947	851	12.7	0.90000	0.00109	1
15,336	0.1910	277	9.8	0.98197	0.00383	121
	0.4378	1,516	9.8	0.90116	0.00506	120
	0.9434	7,588	9.8	0.50520	0.00332	119

Both reagent grade and Y-12 waste-stream hypochlorite were tested. No distinction between these materials was made in Tables 3.1 to 3.5 for the reason that no distinction in degradability was demonstrated with comparable excess NaOH. Table 3.6 shows the correlation between the values predicted by our model and the measured values for upflow operation at 55 and 70 °C. Tables 3.7, 3.8, and 3.9 show little difference degradability even under different process arrangements.

Increasing pH of the feed decreases the fraction NaOCl decomposed (calculated fraction as of Cl^- removed). Because of process stream temperatures in chlorine plants, Pennwalt did little investigation at temperatures below 55°C. Systems under consideration would be considerably simpler to design and build if constant elevated heat were not required for effective operation. However, at relatively low flow rates, it is possible to get over 99% hypochlorite conversion at 25°C.

It is important to remember that 25°C runs were cooled, not heated, to constant temperature: the conversion of hypochlorite heats the solution around 1.4°C for each percent NaOCl converted, increasing the catalyst temperature a corresponding amount. This is particularly significant with a concentrated NaOCl feed.

Table 3.2. Upflow runs at 40°C using Pennwalt catalyst

Feed Cl mg/l	Feed Rate ml/s	Effluent Cl mg/l	Feed pH	Fraction Cl Removed s^{-1}	Measured Reaction Rate s^{-1}	Run No.
7,393	0.0717	10	13.5	0.99866	0.00237	53
	0.1873	535	13.5	0.92767	0.00246	52
	0.4237	2,284	13.5	0.69113	0.00249	51
	0.7353	3,858	13.5	0.47818	0.00239	50
14,397	0.0777	35	13.5	0.99754	0.00233	46
	0.1983	1,181	13.5	0.91798	0.00248	47
	0.4045	4,567	13.5	0.68276	0.00232	48
	0.7205	8,244	13.5	0.42734	0.00201	49
29,928	0.0746	67	13.5	0.99777	0.00228	42
	0.2302	3,113	13.5	0.89597	0.00260	43
	0.4448	10,851	13.5	0.63744	0.00225	45
	0.7440	17,375	13.5	0.41943	0.00202	44
63,119	0.0336	16	13.5	0.99975	0.00139	40
	0.0774	130	13.5	0.99793	0.00239	41
	0.1801	3,844	13.5	0.93910	0.00252	37
	0.4032	17,872	13.5	0.71685	0.00254	39
	0.6410	38,439	13.5	0.39101	0.00159	38

As shown in Table 3.2, decreasing the pH of 30°C samples, like 25°C samples, significantly increased the fraction of hypochlorite decomposd for a given flowrate. At this low temperature, appreciable amounts of hypochlorite, generally over 99% at very low flow rates, were converted, even at high pH. At 3% or less, hypochlorite concentrations appeared to have little effect on its conversion, which was largely a function of flow rate through the column. At 5%, the rate of reaction dropped somewhat for a given flow, probably due to vigorous gas formation characteristic of these catalytic units.

Runs at 55°C and 70°C were performed both as a test of the Pennwalt model based on pilot-scale operations in their production facility and to see if increasing temperature would provide the type of performance increase predicted by textbook chemistry. These runs are summarized in Tables 3.3 and 3.4. As shown in Table 3.5, data was also taken across an extended period to see if there was a noticeable change in performance. After 10 days of operation, there was a mild decrease, about 25%, in effluent hypochlorite concentration. This could indicate a slow improvement in catalyst effectiveness, or might be due to the synergistic effect of any entrained metal oxide particles.

The Pennwalt pilot model was expressed as

$$k = 0.0400 + 0.000515\,T - 0.0046\,pH\,, \tag{1}$$

where k is the first-order reaction rate, T is the temperature in °C, and pH is the pH at the inlet to the bed (Hodges 1986). The necessary catalyst bed volume was determined from

$$F_{converted} = 1 - e^{-k\theta}\,, \tag{2}$$

where F is the fraction of the NaOCl to be decomposed and θ is the empty bed residence time

Table 3.3. Upflow runs at 55°C using Pennwalt catalyst

Feed Cl mg/l	Feed Rate ml/s	Effluent Cl mg/l	Feed pH	Fraction Cl Removed	Measured Reaction Rate s^{-1}	Pennwalt Model Rate s^{-1}	Run No.
8,156	0.0166		12.4			0.01036	6
	0.0774		13.1			0.00760	7
	0.4188	977	13.2	0.88017	0.00444	0.00760	9
8,227	0.1969	24	13.2	0.99707	0.00573	0.00760	8
8,333	0.7082	2,688	13.2	0.67745	0.00400	0.00760	10
	0.8961	3,759	13.3	0.54894	0.00356	0.00760	11
15,531	0.1987	6	11.5	0.99963	0.00786	0.01496	56
	0.4401	102	11.7	0.99342	0.01105	0.01496	55
	0.8741	1,404	11.7	0.90959	0.01049	0.01496	54
16,312	0.6983	5,709	13.5	0.65000	0.00366	0.00622	13
16,418	0.0792	4	13.5	0.99974	0.00327	0.00622	14
16,666	0.1752	104	13.5	0.99379	0.00445	0.00622	15
	1.0000	8,191	13.5	0.50851	0.00355	0.00622	12
31,701	0.2021	16	11.8	0.99951	0.00769	0.01404	63
	0.4139	95	11.9	0.99700	0.01201	0.01404	62
	0.8532	2,652	11.8	0.91633	0.01057	0.01404	64
32,552	0.0775	7	13.5	0.99978	0.00326	0.00622	17
32,694	0.8929	16,347	13.5	0.50000	0.00309	0.00622	19
32,765	0.1860	176	13.4	0.99463	0.00486	0.00622	16
	0.3644	956	13.5	0.97082	0.00643	0.00622	18
65,246	0.8929	24,822	13.5	0.61957	0.00431	0.00577	20
65,388	0.4378	6,986	13.5	0.89317	0.00489	0.00577	21
72,338	0.0696	16	13.5	0.99978	0.00294	0.00577	23
	0.1435	111	13.4	0.99847	0.00465	0.00577	22
98,862	0.0770	14	13.4	0.99986	0.00340	0.00622	68
	0.1955	521	13.4	0.99473	0.00512	0.00622	66
	0.3834	5,326	13.4	0.94613	0.00559	0.00622	67
	0.8503	36,134	13.5	0.63451	0.00428	0.00622	65

in seconds. The flow for θ s then determines the bed volume and weight based on the catalyst density (0.94 g/ml).

For the most part, however, the Pennwalt model poorly reflected the observed system reaction rates and was really considered applicable only to streams containing ≈1.8% hypochlorite expressed as Cl^- and temperatures ranging from 55 to 85 °C.

As shown in Tables 3.3 and 3.4, increasing temperature provided a considerable increase in the rate of reaction and the fraction of hypochlorite removed from a stream, regardless of concentration. At 70°C, mid-range flow rates gave better than 99% hypochlorite removals, even for concentrated, high pH streams. Several linear models similar to the Pennwalt model were fit to the observed data at 55 and 70°C. Using the same model as Pennwalt, a least squares fit to the data in Tables 3 and 4 gives

Table 3.4. Upflow runs at 70°C using Pennwalt catalyst

Feed Cl mg/l	Feed Rate ml/s	Effluent Cl mg/l	Feed pH	Fraction Cl Removed	Measured Reaction Rate s^{-1}	Pennwalt Model Rate s^{-1}	Run No.
916	0.3259	26	13.8	0.97213	0.00583	0.01257	100
9,078	0.1933	7	13.5	0.99922	0.00691	0.01395	36
	0.4098	430	13.5	0.95266	0.00624	0.01395	35
	0.7987	2,482	13.5	0.72656	0.00517	0.01395	34
13,191	0.8306	2,908	13.8	0.77957	0.00627	0.01257	101
15,531	0.1969	10	11.5	0.99936	0.00723	0.02269	57
	0.4078	11	11.6	0.99927	0.01471	0.02269	58
	0.8091	167	11.6	0.98922	0.01831	0.02269	59
18,865	0.2232	24	13.5	0.99872	0.00743	0.01395	32
	0.4425	1,294	14.5	0.93139	0.00592	0.01395	30
	0.8065	4,752	13.5	0.74812	0.00555	0.01395	33
	0.8532	5,674	13.5	0.69925	0.00512	0.01395	31
31,701	0.4105	13	11.9	0.99960	0.01603	0.02177	61
	0.7862	403	11.9	0.98729	0.01714	0.02177	60
36,524	0.4587	1,294	13.5	0.96456	0.00765	0.01395	29
38,651	0.1848	9	13.5	0.99978	0.00777	0.01395	27
	0.6925	6,223	13.5	0.83899	0.00632	0.01395	28
70,920	0.8039	15,851	13.5	0.77650	0.00602	0.01395	25
71,062	0.1860	27	13.5	0.99962	0.00732	0.01395	26
72,622	0.4762	2,308	13.5	0.96821	0.00820	0.01349	24
	0.3259	916	13.8	0.98819	0.00723	0.01257	100
	0.8306	13,191	13.8	0.82998	0.00735	0.01257	101
98,862	0.0747	10	13.4	0.99990	0.00344	0.01395	69
	0.2090	26	13.4	0.99974	0.00863	0.01395	70
	0.4105	1,191	13.5	0.98795	0.00906	0.01395	71
	0.7062	14,716	13.5	0.85115	0.00672	0.01395	72

Table 3.5. Extended run at 70°C using Pennwalt catalyst (Feed concentration 98,862 mg/l Cl)

Elapsed Time h	Feed Rate ml/s	Effluent Cl mg/l	Feed pH	Fraction Cl Removed	Measured Reaction Rate s^{-1}	Pennwalt Model Rate s^{-1}	Run No.
0	0.2465	50	13.4	0.99950	0.00936	0.01395	73
24	0.2390	43	13.5	0.99957	0.00925	0.01395	74
50	0.2330	40	13.5	0.99960	0.00910	0.01395	75
74	0.2117	40	13.5	0.99960	0.00827	0.01395	76
97	0.2163	33	13.5	0.99967	0.00866	0.01395	77
146	0.2135	38	13.5	0.99961	0.00838	0.01395	78
169	0.2279	40	13.5	0.99960	0.00890	0.01395	79
194	0.2232	37	13.5	0.99963	0.00880	0.01395	80
240	0.2203	37	13.5	0.99963	0.00868	0.01395	81

Table 3.6. Model goodness-of-fit for results at 55 and 70°C

Temperature °C	Feed Cl mg/l	Feed Rate ml/s	Effluent Cl mg/l	Feed pH	Measured Reaction Rate s^{-1}	Predicted Reaction Rate s^{-1}	Residual Difference s^{-1}	Lower 95% CL on Mean s^{-1}	Upper 95% CL on Mean s^{-1}	Run No.
55	8,156	0.4188	977	13.2	0.00444	0.00471	−0.00027	0.00382	0.00560	9
	8,227	0.1969	24	13.2	0.00573	0.00425	0.00148	0.00336	0.00513	8
	8,333	0.7082	2,688	13.2	0.00400	0.00488	−0.00088	0.00395	0.00581	10
		0.8961	3,759	13.3	0.00356	0.00493	−0.00137	0.00398	0.00588	11
	15,531	0.1987	6	11.5	0.00786	0.01053	−0.00268	0.00931	0.01176	56
		0.4401	102	11.7	0.01105	0.01101	0.00003	0.00981	0.01220	55
		0.8741	1,404	11.7	0.01049	0.01120	−0.00071	0.00998	0.01243	54
	16,312	0.6983	5,709	13.5	0.00366	0.00390	−0.00023	0.00292	0.00487	13
	16,418	0.0792	4	13.5	0.00327	0.00197	0.00129	0.00041	0.00354	14
	16,666	0.1752	104	13.5	0.00445	0.00317	0.00127	0.00226	0.00408	15
		1.0000	8,191	13.5	0.00355	0.00398	−0.00043	0.00297	0.00498	12
	31,701	0.2021	16	11.8	0.00769	0.01012	−0.00243	0.00900	0.01124	63
		0.4139	95	11.9	0.01201	0.01056	0.00145	0.00944	0.01167	62
		0.8532	2,652	11.8	0.01057	0.01077	−0.00020	0.00961	0.01193	64
	32,552	0.0775	7	13.5	0.00326	0.00226	0.00099	0.00076	0.00376	17
	32,694	0.8929	16,347	13.5	0.00309	0.00429	−0.00120	0.00334	0.00525	19
	32,765	0.1860	176	13.4	0.00486	0.00356	0.00128	0.00276	0.00436	16
		0.3644	956	13.5	0.00643	0.00402	0.00241	0.00318	0.00486	18
	65,246	0.8929	24,822	13.5	0.00431	0.00460	−0.00028	0.00355	0.00564	20
	65,388	0.4378	6,986	13.5	0.00489	0.00440	0.00048	0.00345	0.00535	21
	72,338	0.0696	16	13.5	0.00294	0.00246	0.00046	0.00080	0.00406	23
		0.1435	111	13.4	0.00465	0.00374	0.00090	0.00286	0.00461	22
	98,862	0.0770	14	13.4	0.00340	0.00364	−0.00024	0.00216	0.00512	68
		0.1955	521	13.4	0.00512	0.00500	0.00012	0.00394	0.00605	66
		0.3834	5,326	13.4	0.00559	0.00543	0.00016	0.00425	0.00660	67
		0.8503	36,134	13.5	0.00428	0.00567	−0.00140	0.00438	0.00696	65
70	916	0.3259	26	13.8	0.00583	0.00507	0.00075	0.00391	0.00623	100
	9,078	0.1933	7	13.5	0.00691	0.00603	0.00087	0.00498	0.00708	36
		0.4098	430	13.5	0.00624	0.00650	−0.00026	0.00554	0.00747	35
		0.7987	2,482	13.5	0.00517	0.00671	−0.00153	0.00572	0.00769	34
	13,191	0.8306	2,908	13.8	0.00627	0.00565	0.00061	0.00460	0.00671	101
	15,531	0.1969	10	11.5	0.00723	0.01345	−0.00622	0.01208	0.01483	57
		0.4078	11	11.6	0.01471	0.01391	0.00079	0.01263	0.01518	58
		0.8091	167	11.6	0.01831	0.01412	0.00418	0.01285	0.01538	59
	18,865	0.2232	24	13.5	0.00743	0.00636	0.00106	0.00545	0.00726	32
		0.4425	1,294	14.5	0.00592	0.00674	−0.00082	0.00587	0.00761	30
		0.8065	4,752	13.5	0.00555	0.00691	−0.00136	0.00602	0.00781	33
		0.8532	5,674	13.5	0.00512	0.00693	−0.00180	0.00603	0.00782	31
	31,701	0.4105	13	11.9	0.01603	0.01348	0.00254	0.01234	0.01463	61
		0.7862	403	11.9	0.01714	0.01368	0.00345	0.01253	0.01483	60
	36,524	0.4587	1,294	13.5	0.00765	0.00712	0.00052	0.00639	0.00786	29
	38,651	0.1848	9	13.5	0.00777	0.00661	0.00115	0.00583	0.00739	27
		0.6925	6,223	13.5	0.00632	0.00729	−0.00098	0.00654	0.00805	28
	70,920	0.8039	15,851	13.5	0.00602	0.00801	−0.00199	0.00723	0.00878	25
	71,062	0.1860	27	13.5	0.00732	0.00730	0.00001	0.00661	0.00798	26
	72,622	0.4762	2,308	13.5	0.00820	0.00751	0.00068	0.00678	0.00825	24
	98,862	0.0747	10	13.4	0.00344	0.00650	−0.00306	0.00493	0.00807	69
		0.2090	26	13.4	0.00863	0.00798	0.00063	0.00715	0.00881	70
		0.2117	40	13.5	0.00827	0.00799	0.00027	0.00716	0.00882	76
		0.2135	38	13.5	0.00838	0.00800	0.00037	0.00717	0.00883	78
		0.2163	33	13.5	0.00866	0.00801	0.00064	0.00718	0.00884	77
		0.2232	37	13.5	0.00880	0.00804	0.00076	0.00720	0.00887	80
		0.2279	40	13.5	0.00890	0.00805	0.00084	0.00722	0.00888	79
		0.2330	40	13.5	0.00910	0.00807	0.00102	0.00724	0.00890	75
		0.2390	43	13.5	0.00925	0.00809	0.00116	0.00725	0.00892	74
		0.2465	50	13.4	0.00936	0.00811	0.00124	0.00727	0.00894	73
		0.4105	1,191	13.5	0.00906	0.00839	0.00066	0.00749	0.00928	71
		0.7062	14,716	13.5	0.00672	0.00856	−0.00184	0.00760	0.00953	72

Table 3.7. Typical recirculation run at 70°C using Pennwalt catalyst (Reservoir volume 2 liters with starting feed Cl concentration 65,300 mg/l)

Total Elapsed Time h	Feed Tank Cl mg/l	Flow Rate ml/s	Return Feed Cl mg/l	Feed pH	Fraction Cl Removed	Measured Reaction Rate s^{-1}
0.5	14,525	0.9294	4,268	13.8	0.70615	0.00569
1.0	5,503	0.9294	1,532	13.8	0.72153	0.00593
2.0	1,305	0.9294	205	13.8	0.84275	0.00859
3.0	321	0.9294	86	13.8	0.73170	0.00611
4.0	25	0.9294	4	13.8	0.85000	0.00881
6.3	1	0.9294		13.8		
8.0		0.9294		13.8		

Table 3.8. Two-stage runs at 70°C using Pennwalt catalyst

Colunn Stage No.	Feed Cl mg/l	Feed Rate ml/s	Effluent Cl mg/l	Feed pH	Fraction Cl Removed	Measured Reaction Rate s^{-1}	Run No.	
1	67,584	0.1838	1	13.8	0.99998	0.01005	0.01257	102
2				13.8			0.01257	
1	67,584	0.3259	771	13.8	0.98859	0.00728	0.01257	100
2			21	13.8	0.97307	0.00588	0.01257	
1	67,584	0.8306	11,104	13.8	0.83571	0.00749	0.01257	101
2			2,448	13.8	0.78699	0.00642	0.01257	

Table 3.9. Downflow runs at 70°C using Pennwalt catalyst

Feed Cl, mg/l	Feed Rate, ml/s	Effluent Cl mg/l	Feed pH	Fraction Cl Removed	Measured Reaction Rate s^{-1}	Run No.
67,584	0.4052	1,546	13.8	0.97712	0.00765	105
	0.5353	4,537	13.8	0.93287	0.00722	106

$$k = 0.0466 + 0.000210\ T - 0.0004\ pH. \quad (3)$$

with a multiple correlation coefficient of .70 which means that 70% of the variation of k was accounted for in the model in Eq 3. Since feed concentrations and fractions removed in excess of those investigated by Pennwalt were considered, the additional variables Cl^- feed concentration, C_f and empty-column residence time, θ were included in the model to give

$$k = 0.0447 + 0.000195\ T - 0.0038\ pH + 2.10\times10^{-8}\ C_f - 8.61\times10^{-7}\ \theta\ . \quad (4)$$

where the multiple correlation coefficient increased to 0.75. Estimates of error on the predicted rate coefficients at individual observed values can be are presented in Table 3.6. As can be seen in Tables 3.3 and 3.4, the predicted rate coefficients from Eq. 4 are much less than suggested by Pennwalt: thus more catalyst is required for a given application.

The fall in hypochlorite concentration with time during a typical recirculation run is given in Table 3.7. Several recirculation runs were made. In all cases, hypochlorite solution was pumped from a stirred reservoir through a catalyst column, debubled, and pumped back to the stirred reservoir. Samples were taken regularly enough to get a good curve for hypochlorite degradation. This type of a system could be used with, for example, a tank of hypochlorite not meeting disposal or discharge standards: a pump culd be attached, and the contents of the tank pumped through a catalyst column until the hypochlorite reached a satisfactory level. However, as shown in Table 3.7, satisfactory results require the size of the column to be about 10% of the size of the tank, at an empty column residence time of three m (actual residence <1 m). These constraints will probably preclude use of such as system.

A double column system was considered because it was thought likely that it could, by decreasing mixing (bubbles) in the second column, significantly improve process efficiency. As shown in Table 3.8, the results obtained with double column systems were similar to those obtained with single column systems, and, unfortunately, the flow control for these systems is more complicated and difficult.

In the hopes of dealing with the bubble problem, another approach, downflow liquid continuous operation of a single column, was also attempted. As shown in Table 3.9, this produced results similar to those obtained with single column upflow operation, probably due to bubble entrainment. It is possible that downflow gas continuous operation would provide the desired gas removal and process simplicity. However, at present the Pennwalt catalyst is not available in particles large enough to permit gas continuous downflow operation. Pennwalt indicates an inability to make such a material due to blinding of the catalyst with resin on extrusion.

In summary, the results obtained indicate that about the same rate constants are obtained regardless of the flow configuration.

4. Discussion and Recommendations

This report has concentrated primarily on the Kynar-cobalt oxide catalyst developed and patented by Pennwalt. Other catalyst systems have also been investigated, and these will be covered in separate reports. Both catalyst and computer model, although marketed by Pennwalt to outside companies, were developed to fit Pennwalt facilities. This is reflected in temperature, process stream concentration, and unit process design incorporated into the model, and in the present modified composition of the catalyst pellets themselves (Hodges 1985). For these reasons, the model developed by Pennwalt staff was overoptimistic, by a factor of two or three, on the amount of catalyst that was required to treat process streams in the composition and temperature ranges that we investigated. A comparison of the catalyst activity as measured by Pennwalt and by us in laboratory size columns is presented in Fig. 4.1 (left). Even when limited to Pennwalt specified conditions, the Pennwalt model still under predicted catalyst requirements by a factor of 2 or 3 times.

ORNL-DWG. 86-14953

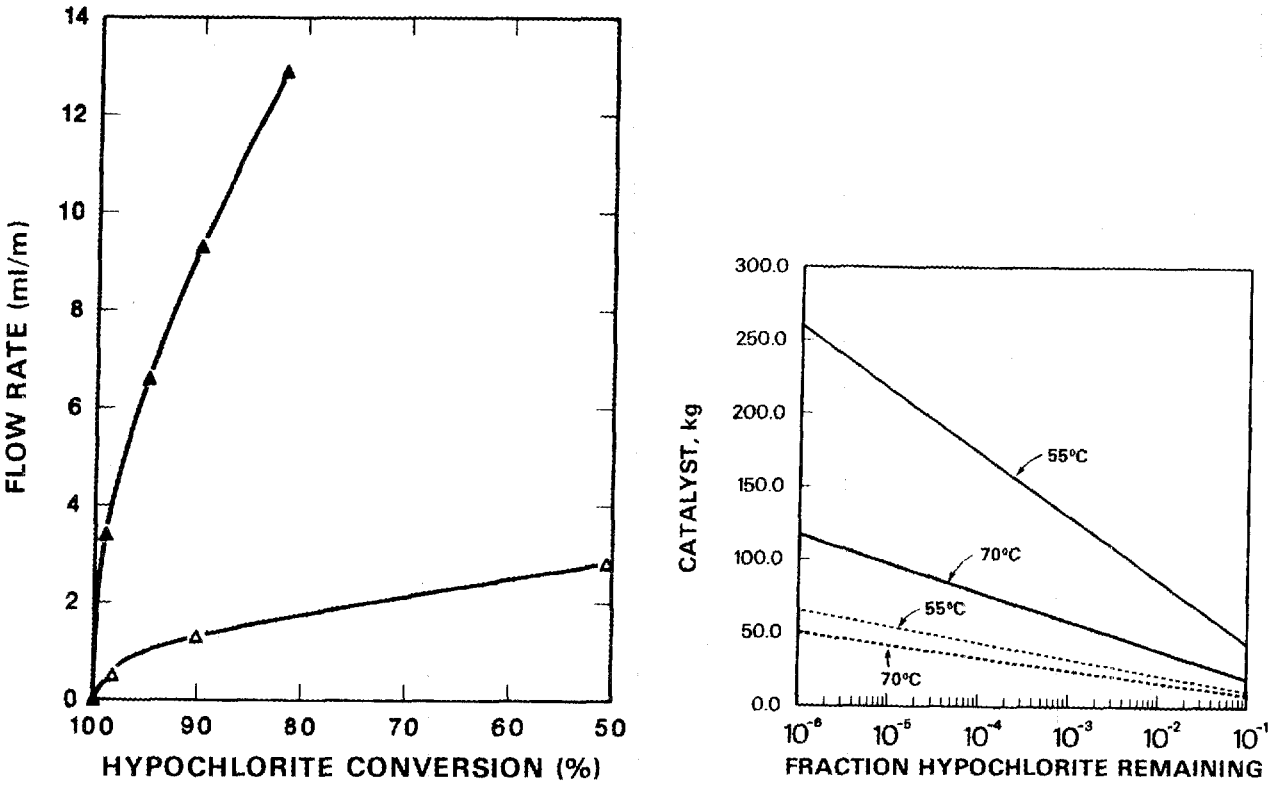

Fig. 4.1. Left: Comparison of catalyst activity as measured by Pennwalt (▲) and by us (△). Right: Catalyst needed to treat 1,500 gallons/day of hypochlorite waste at pH 11 (dashed) and pH 13.5 (solid) at temperatures of 55 and 70 °C from Eq. 4.

The modelling problem was solved by refitting the parameters used by Pennwalt to the data we obtained using the SAS generalized least squares routines. This model was based on a much wider range of operating conditions than those used by Pennwalt, and fitted data whose high pH and high hypochlorite concentration were outside of Pennwalt experience. This data covers process conditions likely to be encountered in Oak Ridge.

Based on data obtained and the models developed, there are several trade-offs to consider in process design and operation. The most fundamental of these are changes which affect catalyst life and efficiency. Since it is formed out of pressed cobalt oxide and Kynar, molded and then cracked, with a fairly high porosity, hypochlorite can diffuse into the middle of catalyst particles. This increases the activity, but also permits generation of oxygen gas inside the particles. At high hypochlorite concentrations generation of internal oxygen gas bubbles can cause the catalyst particles to explode into smaller fragments. These may either form a sludge, causing a need for filtration or settling, or simply wash out of the system. This problem caused Pennwalt to reformulate their catalyst in response to a hypochlorite concentration change from 1.0 to 1.8%. During high hypochlorite runs, especially at high temperatures, the catalyst degraded visibly. Since weighed catalyst was used in our bench scale columns, we were able to measure catalyst attrition across the experimental period. Total attrition amounted to approximately 0.5 gram per gallon of ‡5% hypochlorite solution. This is a process cost, assuming $50 per lb catalyst, of around $0.055 per gallon. High attrition would also force process designs in which the catalyst was readily replaced or used as a powder.

Catalyst attrition occurs simply in response to rapid gas generation, which occurs at high loading rates. It doesn't make any difference whether the loading is volumetric or concentration, or whether the gas is generated in response to low pH or high temperature. A really high efficiency process which generates a lot of gas per unit of bed volume will simply degrade the catalyst at a faster rate than a conservative design.

A number of other trade-offs appear. For example, catalyst efficiency increases with increasing temperature and decreasing pH. Both of these require an extra operation: heating or pH adjustment, and produce regularly occurring costs, energy and chemicals. Both require some instrumentation. However, in each case, the reaction rate is higher, as can be seen from Fig. 4.1 (right). For the Pennwalt catalyst tested, an operating temperature above 50 °C, is probably required to provide reasonable efficiency. Higher operating temperatures would, of course, increase either the loading or degree of hypochlorite reduction. Maximum recommended catalyst temperature is 85 °C. These trade-offs should be considered.

Metallic impurities are, surprisingly, not a process problem, but an advantage. As reported by several different investigators, mixed metallic oxide systems containing transition metal oxides are often more efficient than those containing a single metallic oxide. The major advantage conferred by mixed, rather than single, oxide systems is broadening of operating parameter ranges, including pH, temperature, and concentration. Metallic oxide impurities collected in operating catalyst columns may account for part of the observed increase in operating efficiency with time. However, disposal of heavy metals resident in resins and the gradual leaching of these metals in response to changes in operating conditions may pose effluent disposal problems.

Previous investigations have indicated a potential, but to date uninvestigated, problem: storage of catalyst between uses. In the case of strictly metal oxide catalysts, some investigators have reported a loss of catalyst activity on drying and storage after use. However, other investigators

who stored catalyst as a slurry were able to reuse the material several times with only minor loss of activity. We found no problems with our bench catalysts, but did store them wet between uses. We would suggest that unused catalyst columns be filled with a solution above pH 9 or 9.5 that is unlikely to react with the cobalt oxide. We would also, based on our experience, assume that a period of 1 or 2 h is required to reach full activity after a several days' storage, and it would be reasonable to start up with the ability to reprocess the effluent if necessary.

Based on the experimental data in Chapter 3, a number of different flow arrangements can be used. These include straight through upflow operation, downflow operation, two column series operation, and recirculation. The siting of the unit is also open. It may be advantageous to site a unit at the scrubber itself so that low levels of hypochlorite can be removed continuously. This would provide the process advantage that the unit would be located in a controlled environment. In winter, any process heating requirements would be considerably lessened, and the equipment would not need steam tracing. To prevent catalyst degradation during startup, shutdowns, etc., some control of catalysis through flow control, hypochlorite concentration, or temperature would needed. A second stage cleanup might be required to meet EPA discharge requirements economically.

A once-through single column upflow process arrangement was hard to beat. Downflow liquid continuous modes were tried, but bubble entrainment caused process efficiencies roughly equal to those observed with upflow arrangements. In a similar fashion, two column arrangements were roughly equal in efficiency to a once-through upflow. However, for both the downflow and two column systems, process flow management was more complicated than it is for a simple upflow system. Recirculation was tested in the hopes of being able to recirculate to a storage tank, with release when the hypochlorite reached acceptable levels. Unfortunately, the flow restrictions on the catalyst bed made recirculation practical only when the flowrate was high enough to give frequent storage tank turnovers. This implied a large catalyst bed at reasonable flow velocities or several days to process several thousand gallons. We did not test downflow, gas continuous systems, which seem likely to have a considerable process advantage, because catalyst pellets available only in very small sizes.

It is possible that Oak Ridge process streams will contain small amounts of mercury, possibly on the order of a fraction of a part per million. This could limit disposal options; however, it will not decrease catalyst activity: as noted in the literature survey, oxides of mercury are reasonably effective in catalyzing hypochlorite degradation. The major question is long term residence, since it is reasonable to expect a catalyst column to last through several months of operation, and ultimate disposal of the catalyst. It should also be possible to interface a catalyst column with most of the current mercury removal systems, using some of the same process control steps, such as pH control, to optimize both processes. If mercury removal is a major concern, this should be evaluated reasonably carefully. A tentative estimation of mercury removal could be made using AA analysis of samples retained during the bench experiments.

Several options could provide interesting alternatives for future process evaluation. Based on literature references, it appears likely that the same catalyst system can be used to cocurrently remove hypochlorite and cyanide wastes. This could be particularly useful, but the information should be verified due to the potential hazard involved.

The Pennwalt catalyst is a major process cost, and it forces several process requirements, such as heating. The availability of a catalyst which was effective at lower temperatures, cost less,

and was more readily available would contribute considerably to the ability to design an efficient, inexpensive catalyst system. For example, it could permit development of an effective process design for use in conjunction with chlorine scrubbers at their ambient process temperature.

Chapter 5. Process Implications

The Pennwalt catalyst is able to satisfactorily decompose hypochlorite to chloride and oxygen at temperatures between 55 and 70°C. Efficiencies higher than 99% could be obtained for relatively low flow rates at 55°C and for mid-range flow rates at 70°C. Process efficiency increased as influent pH decreased and as temperature increased. Based on bench data, it appears possible to design a single pass column for operation between 55 and 70°C which will reduce hypochlorite concentration below the amount detected by the starch-iodide titration method used for hypochlorite evaluation. With the possible exception of influent pH control, no input chemicals are required, and the process can be readily monitored by chemical operators using the same simple tests described in *Materials and Methods*.

Several process problems need to be considered in choosing the best process design. Catalyst attrition is, in our estimation, a major problem. Bench tests showed a catalyst loss of approximately 0.5 gram per gal of concentrated hypochlorite solution processed, a cost of roughly $55 per 1000 gal processed. Catalyst attrition is thought to result from disintegration of the Kynar-CoO particle by oxygen trapped in its pores. The rate of catalyst degradation can be limited by decreasing hypochlorite concentration, or using a lower process temperature. Harshaw-Filtrol has also indicated a willingness to produce a catalyst with more Kynar binder. A high-Kynar material should be less sensitive to disintegration. However, it will probably cost more per unit weight or unit activity, and a larger bed size will probably be required.

Because of catalyst attrition, it is important to provide for reasonably easy access to the catalyst bed so that its condition can be evaluated and any reloading or resizing can be performed. This should be a major design consideration. Provision should also be made for purchase and storage of a replacement supply of the catalyst itself, since it is made by a single manufacturer. Since the material described in the Pennwalt patent is no longer that supplied by Pennwalt, it could be difficult to duplicate at Y-12 in the event of a catalyst production problem.

The Pennwalt catalyst at bench scale requires a short conditioning period before NaOCl reduction stabilizes. Shorter conditioning periods are required prior to column reuse after storage. However, provision should be made for determination, collection, and recycle of unacceptable effluent.

Chapter 6. Materials and Methods

Catalyst Columns.

A jacketed column 25 mm diameter and 450 mm long was tared and filled with catalyst particles. After these were tamped down well, the column was weighed and a few glass beads or 6 mm raschig rings were added at the top. The size distribution of the catalyst used is given in Table 6.1. After filling, the column cap was screwed down. The column free volume was filled with distilled water and the increased weight was measured. During operation, column temperature was controlled using a circulating water bath.

Table 6.1. Pennwalt catalyst screen-size analysis (Lot 4 D-4906-G 4-14)

Mesh-size range	Percent
<4	0.7
4–8	61.8
8–10	26.0
10–14	10.3
>14	1.2

Column startup. Preoperation conditioning is required for consistent column operation. To accomplish this, a column was operated using a mild hypochlorite and caustic solution for a period of at least 24 h at 70°C or 48 h at 55°C.

Column operation. In straight through runs, a column was operated for at least 10 superficial column volumes prior to taking analytical samples. In the case of recirculation runs, samples were taken from both the column and the stirred vessal periodically.

Column Feedstock

Feedstock for earlier runs was prepared using either reagent grade (4 to 6%) NaOCl or Sno Cap bleach, a commercial 10% hypochlorite solution. Reagent 50% or 10 *N* NaOH was added to simulate process streams.

In later runs, scrubber effluent was used as a feedstock. This material was obtained prior to finish filtration, and was allowed to stand, covered, until most of the particulate material settled. Both feedstocks were added to the columns using a peristaltic pump. Flow rate was measured by the amount of time required for effluent to fill a small volumetric flask.

Hypochlorite Determination. Tare a 25 ml volumetric flask, fill with hypochlorite solution and weigh. Determine the weight and density of the solution. Rinse the sample into a 250 ml volumetric flask, and make to volume with distilled water. Invert at least ten times to mix.

In a 250 ml beaker, dissolve 2 g KI crystals and 2 ml concentrated HCl in 50 ml distilled water. Add 10 ml (or other appropriate volume) diluted sample. Titrate with 0.1 *N* $Na_2S_2O_3$ until straw colored. Add 5 ml starch indicator. Titrate until the blue color disappears. The reagents used are all standard reagent grade chemical stores items. The available chlorine in mg/l is calculated by

$$Cl_{avail} = ml\ Na_2S_2O_3 \times N \times 0.03546 \times 10^6 \times 250\ /\ vol_{sample}\ /\ vol_{titrated}\ .$$

where vol_{sample} is the sample aliquot diluted to 250 ml and $vol_{titrated}$ is the volume of the aliquot of the 250 ml diluent acidified and titrated.

Starch indicator. Mix 5 g of starch into a paste and stir into enough boiling distilled water to make approximately 1 liter. Cool and filter.

7. References

Balard, A. R. 1834. Recherches sur la nature des combinaisons de colorantes du chlore. *Annales de Chimie et de Physique* 57: 225-304.

Bidet, A. 1886. Preparation continue de l'oxygene au moyen du chlorure de chaux et de l'oxyde de cobalt. *Bulletin de la Societe Chimique de France* 45: 81-83.

Caldwell, D. L., and R. J. Fuchs, Jr. 1978. Catalytic decomposition of hypochlorite. U. S. patent 4,073,873.

Caldwell, D. L., and M. J. Hazelrigg, Jr. 1982. Substituted cobalt oxide spinels. European patent 61,717.

Caldwell, D. L., and M. J. Hazelrigg, Jr. 1983. Catalytic decomposition of hypochlorite using substituted cobalt oxide spinels. U. S. patent 4,368,110.

Chiba Enso Kagaku K. K. 1981. Hypochlorite decomposition catalyst. Japanese patent 81/656,655.

Ciurlizza, G. A., and L. J. Mojica. 1983. Proposal of a Gompetz mathematical model for the correlation of reaction rate constants with temperature in inorganic reactions. *Acta Mexicana de Ciencia y Technologica* 1: 11-22.

Clark, R. T. 1980. Catalyst for the decomposition of hypochlorite wastes. Paper read at the Chlorine Plant Manager's Seminar, 6 February 1980, New Orleans.

Clark, R. T., and D. M. Gardner. 15 December 1980. Catalyst pellets with binder for deomposition of hypochlorite. U. S. patent 4,400,304.

Clark, R. T., and D. M. Garnder. 1981. Catalyst and methods for decomposing hypochlorite. German patent 3,037,546.

Crawford, R. A., and R. B. Simmons. 1981. Decomposing hypochlorite ion in a basic solution. U. S. patent 4,297,333.

Denisova, A. I., and A. M. Agaltsov. 1970. Catalyst for the decomposition of hypochlorite solutions. U. S. S. R. patent 285,903.

Gay-Lussac, J. L. 1842. Sur les combinacisons du chlore avec les bases. *Compte Rendu* 14: 927-952.

Gerland, B. W. 1891. Some laboratory experiences. *Journal of the Society of Chemical Industry* 10: 25-26.

Gokhale, S. D., and L. L. Frank. 1982. Hypochorite waste management in chlor-alkali industry. In *Waste treatment and utilization,* ed. M. Moo-Young, C. W. Robinson, and G. J. Farquhar, pp. 347-367. New York: Pergamon Press.

Gray, E. T., Jr.; Taylor, R. W., and Margerum, D. W. 1977. Kinetics and mechanisms of the copper-catalyzed decomposition of hypochlorite and hypobromite. Properties of a dimeric copper (III) hydroxide intermediate. *Inorganic Chemistry* 16: 3047-3055.

Hamano, A., and H. Mori. 1977. Activity of metal oxide catalysts. 4. Activity and surface area of transition metal oxide catalysts. *Sasebo Kogyo Koto Senmon Gakko Kenkyu Hokoku 14: 65-72.*

Hamano, A.; Oda, H.; Kurusaki, Y.; and Mori, H. 1985. Activity of metal oxide catalysts. 7. Effect of hydroxide ion concentration of the catalyst on the decomposition of a sodium hypochlorite solution by metal oxides. Kenkyu Hokoku 22: 103-111.

Hodges. J. R. 5 May 1986. Private communication covering Pennwalt design equation for hypochlorite system.

Hoffmann, K. A., and K. Ritter. 1914. Stability and oxidation potential of hypochlorites. *Berichte der Deutschen Chemischen Gesselschaft* 47: 2233-

Howell, O. R. 1923. The catalytic decomposition of sodium hypochlorite by cobalt peroxide. *Proceedings of the Royal Society (London):* 104A: 134-152.

Kind, W. 1922. Bleichschaden in Leinen durch Metallverunreinigungen. *Textilberichte uber Wissenschaft, Industrie und Handel* 3: 131-134.

Kinosz, D. L. 1976. Anti-pollution method. U. S. patent 3,965,249.

Krunchak, V. G. 1974. Effect of metal chlorides on the rate of self-dissociation of solutions of hypochlorite and hypochlorous acid. *Zhurnal Prikladnoi Khimii* 47: 2112-13.

Kurlyandskaya, I. I.; Furman, A. A.; Rogozhina, S. A.; Kucher, V. L.; Antonova, A. N.; and Rabovskii, B. G. 1972. Catalyst for the decomposition of hypochlorite solutions. U. S. S. R. patent 348,223.

Lewis, J. R. 1928. The catalytic decomposition of sodium hypochlorite solutions. I. Mechanism of the reaction. *Journal of Physical Chemistry* 17: 243-254.

Londhe, V. S., and P. R. Kamath. 1975. A note on the catalytic decomposition of waste sodium hypochlorite solution. *Water Research* 9: 1009-1010.

Makarov, S. Z., and S. S. Shraibman. 1956. Acid method for removal of active chlorine in the production of chlorates. *Khimichna Promyshlenost* No. 4: 202-208.

Mitscherlich, E. 1843. Vermischte chemische Beobachtungen *Poggendorff's Annalen der* Physik 58: 468-473.

Mitsubishi Heavy Industries, Ltd. 1981. Treatment of free chlorine containing wastewaters. Japanese Patent 81/108587.

Mori, H., and A. Hamano. 1984. Catalysis of copper, cobalt, and nickel oxides for decomposition of sodium hypocholoride solution at low temperature. Activity of metal oxide catalysts. 6. *Kenkyu Hokoku* 21: 75-78.

Muspratt, M., and E. S. Smith. 1898. Some experiments upon high-strength hypochlorite solutions. *Journal of the Society of Chemical Industry* 17: 1096-1100.

Patel, M. C., and B. N. Mankad. 1954. A note on the effect of salts on the decomposition of sodium hypochlorite. *Journal of the Indian Chemical Society, Industrial and News Edition* 17: 236-237.

Pennwalt Corporation. 16 July 1981. Catalyseur en pastilles comprenant un liant resinique pour la decomposition d'un hypochlorite et son procede d'utilization. Belgian patent 888.204.

Pivovar, A. G.; Akimova, N. A.; Sedova, L. P.; Snurnikova, L. V.; Ovcharenko, V. G.; Nagaets, N. N.; Stavrov, L. P.; and Kozyr, N. G. 1979. Decomposition of calcium hypochlorite. U. S. S. R. patent 670,533.

Tarkovskaya, I. A.; Stavitskaya, S. S.; and Petrenko, T. P. 1979. Study of catalytic acivity of oxidized carbons of different origin in redox reactions. *Adsorbtsiya Adsorbenty* 7: 3-7.

White, A. D. 1903. The action of solutions of bleaching powder and of hypochlorous acid on metals. *Journal of the Society of Chemical Industry* 22: 132-134. U. S. S. R. patent 459,432.

INTERNAL DISTRIBUTION

1-5.	A. L. Compere	19.	K-25 Plant Library
6-10.	W. L. Griffith	20.	ORNL Patent Office
11-15.	W. P. Huxtable	21.	Y-12 Technical Library / Document Reference Station
16.	I. W. Jeter		
17.	J. M. Napier	22.	Laboratory Records - RC
18.	Central Research Library	23-24.	Laboratory Records Department

EXTERNAL DISTRIBUTION

25. Lawrence Wagner, Pennwalt, 900 First Ave., King of Prussia PA 19406-0018.

26-27. Technical Information Center, DOE.

28. Assistant Manager Energy Research and Development, DOE/ORO