A mill survey of oxygen utilization in extraction and delignification processes

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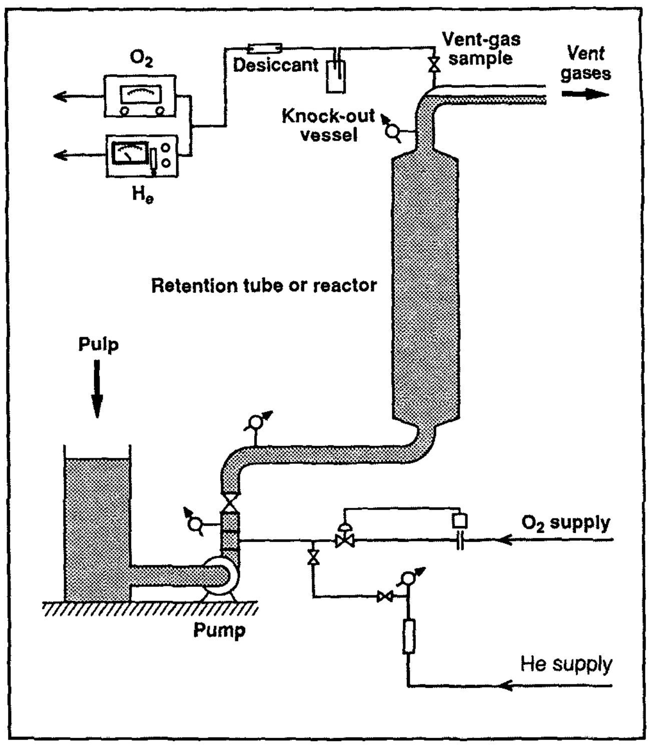
Gas channeling was not severe in the mills studied. Separation of gas from the pulp slurry most likely occurs at the vessel walls.

The first commercial application of oxygen in bleaching was on a high-consistency pulp produced by the Sapoxal process. This initial application, developed by L'Air Liquide in conjunction with Kamyr and SAPPI, was installed in South Africa (*1*). The use of oxygen in bleach plants has greatly increased since then, driven primarily by the pressure of environmental demands. The development of mixers for dispersing oxygen into pulp has spurred the growth of medium-consistency oxygen extraction and delignification processes (*2*).

In all of these processes, the quantity of oxygen added to pulp is measured. However, the amount that is absorbed and reacts is not. This raises the question as to whether enough, or too much oxygen is being added.

Our company has developed a patented method of conducting a mass balance for oxygen (*3*). The method uses helium as a tracer gas. A known quantity of helium is added to the oxygen before it is dispersed in the pulp slurry. The oxygen-containing helium gas is then mixed with pulp, where it is absorbed and reacts. The helium and oxygen concentrations are measured at the end of the process, when the vent gases are released from the pulp slurry. With this information, it is possible to calculate both the vent-gas flow rate and the oxygen flow rate. The flow rates for nitrogen and air can then be estimated, providing the basis for an oxygen mass balance (*4*).

1. Helium addition and vent-gas sampling



Helium tracer test

Helium as a tracer gas

Helium is a nontoxic, nonflammable, chemically inert gas with low solubility in pulp slurries (*5*). Its thermal conductivity is much higher than that of oxygen, nitrogen, or air, so it can be readily detected in the presence of these gases using a portable thermal-conductivity analyzer or gas chromatograph (*6*).

Choice of instruments

A thermal-conductivity analyzer is used for helium gas analysis. The device is calibrated with known mixtures of helium in air at the approximate temperature of the vented gas. A paramagnetic oxygen analyzer is used for oxygen analysis, and it is calibrated with known mixtures of oxygen in air. The flowmeter used to measure the flow of helium added to oxygen is calibrated using pure helium.

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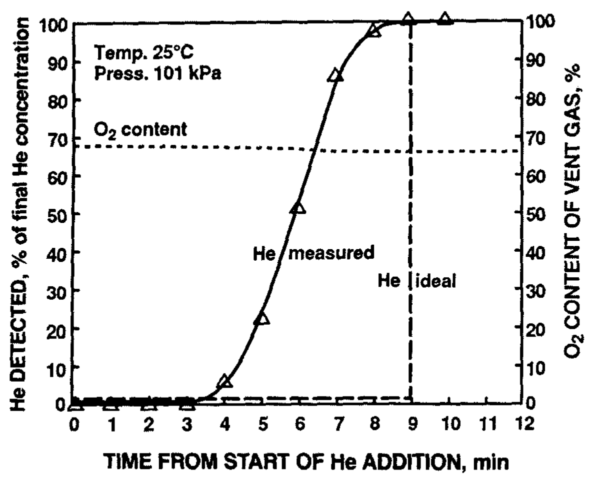
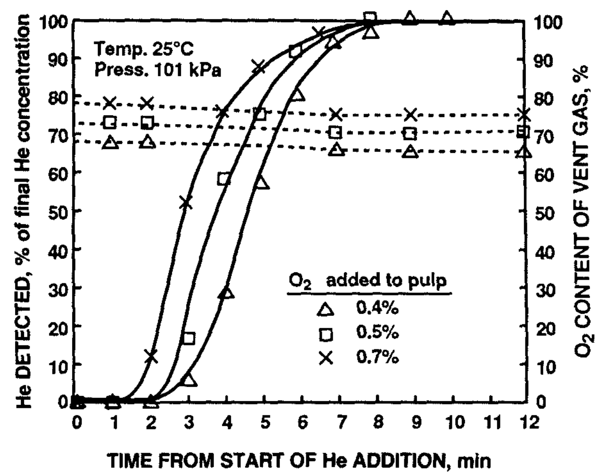
2. Helium breakthrough curve



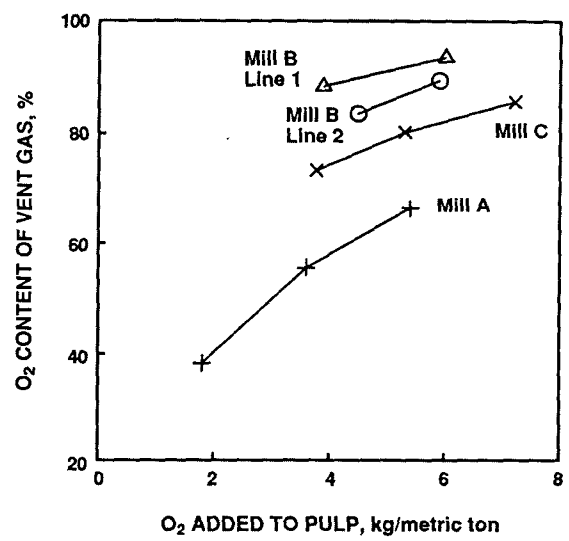
3. Effect of increasing oxygen addition on helium breakthrough curve



I. Operating conditions in three Canadian mills (oxygen extraction process)

		Mill B		
	Mill A	Line 1	Line 2	Mill C
Type of wood	Softwood	Softwood	Softwood	Softwood
Pulp process	Kraft	Kraft	Kraft	Kraft
Pulp consistency, %	10	7.5-10.0	...	11
Caustic added, kg/metric ton	30	...	...	30
Pulp temperature, °C	75	72	72	73
Retention-tube pressure, kPa				
Inlet	500	433	433	461
Outlet	333	233	233	233
Retention-tube residence time, min	9.8	5.5	8.0	11

4. Oxygen content of vent gas as a function of oxygen added to pulp for three Canadian kraft mills



Sampling of vent gases

The sampling point is chosen to be close to the outlet of the retention tube or reactor so that gases are vented under pressure and to avoid the aspiration of air into the sample. The vent gas is cooled and passed into a knock-out vessel, where water droplets are removed from the gas stream, and then through a desiccant. From here, the flow is divided, with one stream passing into the helium analyzer and the other into the oxygen analyzer. **Figure 1** illustrates the locations for helium addition and vent-gas sampling.

Addition of helium to oxygen

High-purity helium gas is added at a known flow rate using the calibrated flowmeter. The gas is added to the oxygen supply line at a point that allows the gases to be thoroughly mixed before being dispersed in the pulp slurry.

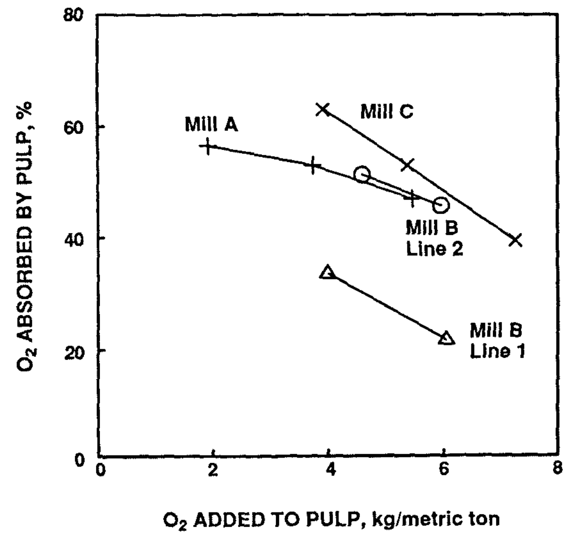
Procedure for carrying out test

Before any helium is added to the system, the helium and oxygen analyzers are installed and readings are monitored. At some predetermined time, the helium flow is started, and readings from both analyzers are recorded at regular intervals, usually every minute. These readings are continued until steady values are obtained, at which point the helium flow is terminated. The helium is purged from the system, and both analyzers are monitored to

II. Air content of pulp slurries in three Canadian mills (oxygen extraction process)

	Mill A	*Mill B* Line 1	*Mill B* Line 2	*Mill C*
Pulp consistency, %	10	7.5-10.0	...	11
Pump	No vacuum degassing	Vacuum degassing	Vacuum degassing	Vacuum degassing
O_2 addition	Mixer	Diffuser	Diffuser	Diffuser
Air in pulp, %	15.8-20.5	3.5-4.4	2.9-3.2	3.7-4.8

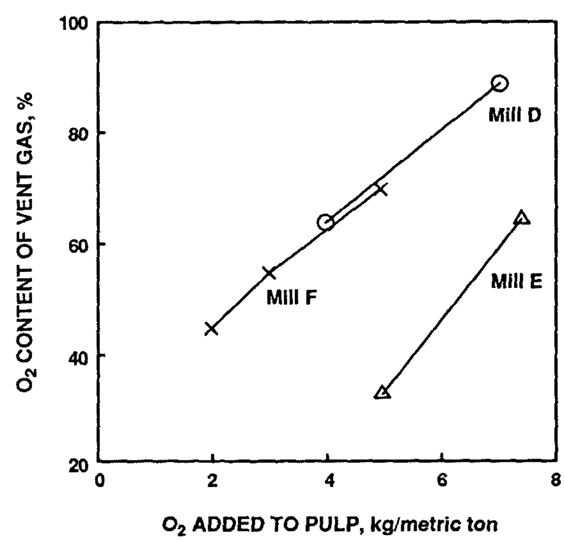
5. Oxygen absorbed by pulp as a function of oxygen added to pulp for three Canadian kraft mills



III. Operating conditions in three U.S. mills (oxygen extraction process)

	Mill D	*Mill E*	*Mill F*
Type of wood	Softwood	Softwood	Hardwood
Pulp process	Kraft	Kraft	Kraft
Pulp consistency, %	10	9-10	12
Caustic added, kg/metric ton	50	...	30
Pulp temperature, °C	60	75	75
Retention-tube pressure, kPa			
Inlet	422	433	200
Outlet	238	100	100
Retention-tube residence time, min	9.9	10.7	10.9

6. Oxygen content of vent gas as a function of oxygen added to pulp for three U.S. kraft mills



verify that the readings are the same as before the test was started.

Helium breakthrough curves

The measurements of helium and oxygen concentrations are plotted against time from the start of helium addition. A typical curve is shown in **Fig. 2**, where the plotted helium concentration is expressed as a percentage of the final helium reading.

In an ideal situation—where gas is very well dispersed and is held in the pulp under plug-flow conditions up the retention tube or reactor—helium will be detected just after an elapsed time corresponding to the hydraulic residence time. This situation is depicted by the "ideal" curve in Fig. 2. In most cases, helium is detected sooner than this, indicating separation of gas from the pulp slurry and some channeling, as shown by the "measured" curve.

Figure 2 also shows that the oxygen content of the gas gradually decreases until it reaches a steady state.

Calculation of oxygen balance

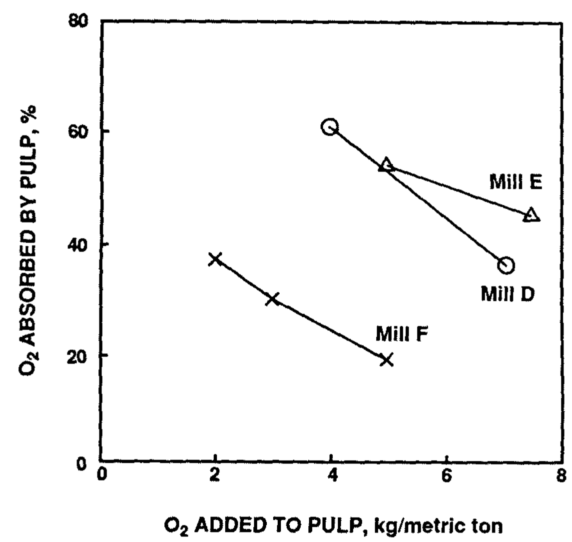
The calculations of oxygen balance are made on a dry-gas-basis reference to standard conditions, with flows for gas and pulp slurry expressed in units of m^3/h.

$$\text{Vent-gas flow} = (100/\text{He concentration (\%) in vent gas}) \times \text{He flow added to pulp} \quad (1)$$

IV. Air content of pulp slurries in three U.S. mills (oxygen extraction process)

	Mill D	*Mill E*	*Mill F*
Pulp consistency, %	10	10	11
Pump	Vacuum degassing	No vacuum degassing	No vacuum degassing
O_2 addition	Mixer	Diffuser	Mixer
Air in pulp, %	0.5-3.8	...	15-16

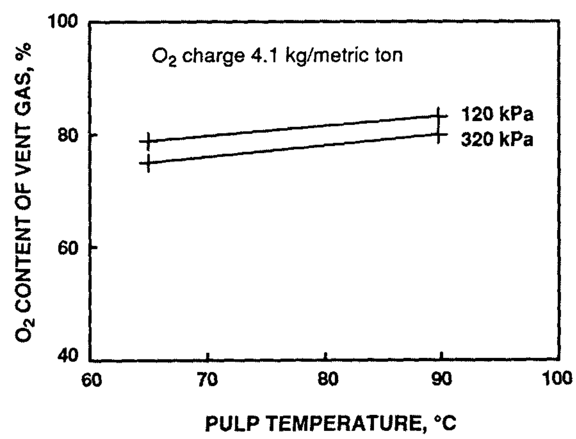
7. Oxygen absorbed by pulp as a function of oxygen added to pulp for three U.S. kraft mills



V. Operating conditions in Swedish mill producing hardwood and softwood kraft pulps (oxygen extraction process)

	Hardwood	*Softwood*
Pulp consistency, %	9	9
Caustic added, kg/metric ton	35	35
Pulp temperature, °C	65-90	65-90
Retention-tube pressure, kPa		
Inlet	220-420	240-405
Outlet	120-320	140-305
Retention-tube residence time, min	10.0	10.0

8. Oxygen content of vent gas as a function of pulp temperature for hardwood kraft pulps at lower and higher retention-tube outlet pressures



$$O_2 \text{ flow in vent gas} = \text{vent-gas flow} \times (O_2 \text{ concentration (\%) in vent gas}/100) \quad (2)$$

Because the vent gas contains only N_2, O_2, and He

$$N_2 \text{ flow} = \text{vent-gas flow} - (O_2 \text{ flow in vent gas} + \text{He flow in vent gas}) \quad (3)$$

Because all nitrogen present is derived from air

$$\text{Air flow} = N_2 \text{ flow}/0.79 \quad (4)$$

Assuming no oxygen was consumed from air,

$$O_2 \text{ flow (unreacted)} = \text{vent-gas flow} - (\text{air flow in vent gas} + \text{He flow in vent gas}) \quad (5)$$

$$O_2 \text{ flow (reacted)} = O_2 \text{ flow added to pulp} - O_2 \text{ flow (unreacted)} \quad (6)$$

$$O_2 \text{ \% (reacted)} = (O_2 \text{ flow (reacted)}/O_2 \text{ flow added to pulp}) \times 100 \quad (7)$$

$$\text{Air in pulp, \%} = [\text{air flow}/(\text{pulp flow} + \text{air flow})] \times 100 \quad (8)$$

Results for oxygen extraction process

Helium tracer tests were carried out in several mills in Canada, the United States, Sweden, and France. The tests were conducted with the objectives of measuring the extent of gas channeling and determining oxygen mass balances.

Helium breakthrough tests

Gas channeling generally was not severe in the mills that were studied. The channeling that was detected is believed to arise from separation of gases from the pulp slurry close to the walls of the vessel. There was no evidence of gas bubbling or "burping" up through the pulp.

Figure 3 illustrates another observed trend: The elapsed time for helium detection decreased as more oxygen was added to the pulp.

Oxygen mass balance

Canadian mills. The operating conditions for three Canadian mills producing softwood kraft pulp are shown in **Table I**. Mill A is located in eastern Canada; Mills B and C are located in western Canada.

Figure 4 shows the oxygen content measured in the vent gas plotted against the oxygen added to the pulp. The trend is the same for all mills: As more oxygen is added to the pulp, the oxygen content of the vent gas increases.

The oxygen concentration in the vent gases was markedly higher for Mills B and C than for Mill A. This was because Mills B and C dispersed the oxygen in the pulp slurry using a pump with a vacuum degassing unit, which removed some of the entrained air. Mill A's pump was not equipped with vacuum degassing, so the pulp contained more air, which diluted the unreacted oxygen in the vent gas. This can be seen in **Table II**, which compares the air content of pulp slurries for the three mills.

Figure 5 shows the percentage of oxygen absorbed by the pulp plotted against the amount of added oxygen. Again, there is a general trend for all the mills: As more oxygen is added to the pulp, the percentage of oxygen absorbed decreases. There is, however, a difference among the mills. Mill B's Line 1 absorbs much less oxygen than Line 2. This is believed to be attributable to a shorter contact time between pulp and oxygen, variations in the quality of the pulp, and other processing differences.

Mill A and Mill B/Line 2 absorbed about the same percentage of oxygen at addition levels of 4-6 kg metric ton. Oxygen absorption for Mill C was slightly higher over the same range of oxygen addition.

U.S. mills. Operating conditions for the three U.S. mills producing kraft pulp are shown in **Table III**. Mill D is located in the west and uses softwood. Mills E and F are located in the southeast and use softwood and hardwood, respectively.

Figure 6 shows oxygen content measured in the vent gas plotted against oxygen added to the pulp. The previously observed trend is evident: As more oxygen is added, the oxygen content in the vent gas rises. For Mill E, the oxygen content of the vent gas is much lower than for Mills D and F. This is because the vent gas from Mill E aspirated air before the oxygen content was measured.

Table IV shows the air content of the pulp slurries for Mills D and F. For Mill D, with a pump equipped with vacuum degassing, the air content is lower. It was not possible to measure the air content for Mill E because the vent gas contained aspirated air.

Figure 7 shows the percentage of oxygen absorbed by the pulp plotted against the amount of added oxygen. The trend is the same for all mills: As more oxygen is added, the percentage absorbed falls.

Mill F, which uses hardwood pulp, shows the lowest percentage of oxygen absorbed. Of the tested mills, Mill F was the only one that used hardwood, so it is not possible to confirm that hardwood pulps absorb less oxygen than softwood pulps.

Swedish mill. Tests at the Swedish mill were carried out to determine the effects of retention-tube pressure and pulp temperature on the amount of oxygen absorbed. The mill produces both hardwood and softwood kraft pulps. Operating conditions for the oxygen extraction process are listed in **Table V** for both hardwood and softwood.

Figure 8 shows the oxygen content of vent gas plotted against pulp temperature for hardwood kraft pulp. The expected result—that increasing pulp temperature would allow more of the oxygen to react, resulting in a decrease in the oxygen content of the vent gas—did not occur. In fact, Fig. 8 shows that the reverse was true, with the oxygen content of the vent gas increasing with pulp temperature. This is because both the air content of the pulp slurry and the vent-gas flow are lower at higher pulp temperatures, increasing the oxygen concentration. **Figure 9** shows a similar trend for softwood pulp at a pressure of 140 kPa, but the trend is reversed at the higher pressure.

Figure 10 shows that hardwood pulp absorbs more oxygen as the pulp temperature is raised from 65°C to 90°C. Increasing the retention-tube pressure increased oxygen absorption uniformly over the same temperature range. **Figure 11** shows similar results for softwood pulp, but in this case, oxygen absorption increased more rapidly at the higher retention-tube pressure.

Table VI shows that in this process—where steam is added to the pulp at the steam mixer ahead of the pump—the air content of both hardwood and softwood pulp slurries decreases when pulp temperature is increased from 65°C to 90°C.

French mill. Operating conditions for a French mill producing softwood sulfite pulp are shown in **Table VII.**

Figure 12 shows the oxygen content of vent gas plotted against the oxygen added to pulp. The usual trend is apparent: As more oxygen is added to the pulp, the oxygen content in the vent gas rises. The air content measured in the pulp is listed in **Table VIII.**

Figure 13 shows the percentage of oxygen absorbed by the pulp plotted against the amount of oxygen added. The same trend is evident, with the percentage of absorbed oxygen decreasing with increasing addition of oxygen. Based on these results, it appears that oxygen utilization is similar for both the sulfite and kraft processes.

Results for oxygen delignification process

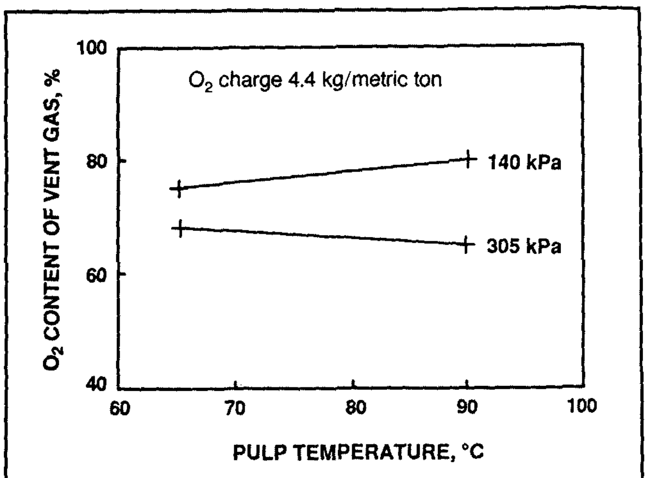
The helium tracer test also was used to carry out a mass balance in the oxygen delignification process. Tests were conducted in a Swedish kraft mill that uses both softwood and hardwood pulps. The operating conditions for the tests are shown in **Table IX**. The air content of the pulp slurries was measured, and the results are shown in **Table X.**

Results of the oxygen mass balance for the hardwood and softwood pulps are shown in **Table XI**. In both cases, the oxygen content of the vent gas leaving the reactor was very low, well below the oxygen content of air. Hence all the oxygen added was consumed, along with some of the oxygen from the air entrained within the pulp slurry.

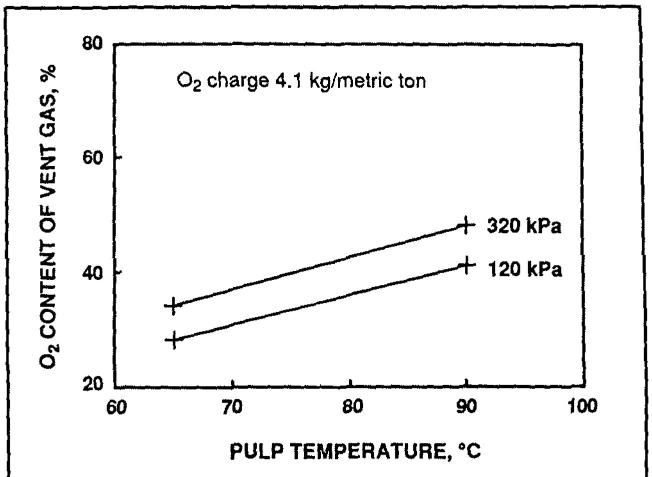
Conclusion

Results of tests conducted at mills in Canada, the United

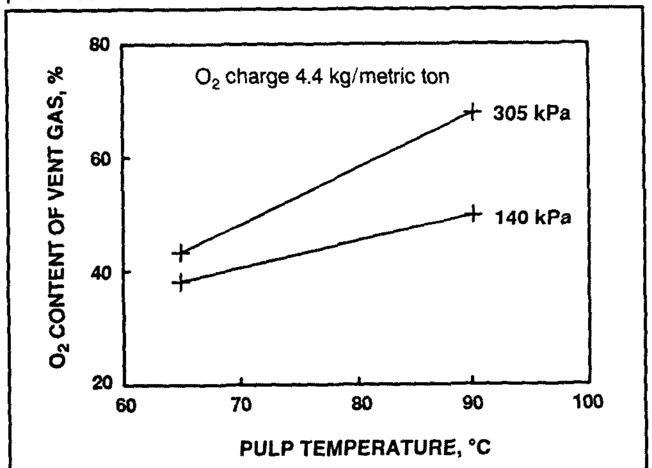
9. Oxygen content of vent gas as a function of pulp temperature for softwood kraft pulps at lower and higher retention-tube outlet pressures



10. Oxygen absorbed by pulp as a function of pulp temperature for hardwood kraft pulps at the lower and higher retention-tube outlet pressures



11. Oxygen absorbed by pulp as a function of pulp temperature for softwood kraft pulps at the lower and higher retention-tube outlet pressures



VI. Air content of pulp slurries in Swedish mill producing hardwood and softwood kraft pulps (oxygen extraction process)

	Hardwood		*Softwood*	
Pulp consistency, %	9		9	
Pump	No vacuum degassing		No vacuum degassing	
O_2 addition	Mixer		Mixer	
Pulp temperature, °C	65	90	65	90
Air in pulp, %	5.1-5.9	2.6-2.8	6.1-9.1	2.9-5.4

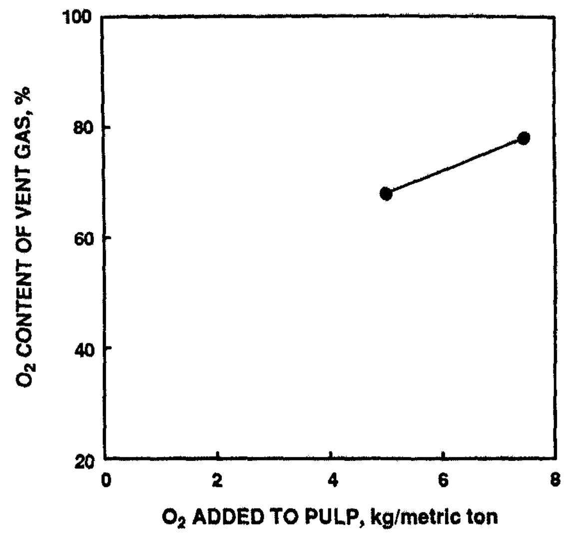
States, Sweden, and France support the following conclusions:

1. For the medium-consistency oxygen extraction process, increasing the quantity of oxygen added to the pulp led to an increase in the oxygen content of the vent gas and a decrease in the percentage of oxygen absorbed by the pulp. Most mills add 4-6 kg O_2/metric ton of pulp, resulting in about 40-60% of the oxygen being absorbed.
2. For the medium-consistency oxygen extraction process, increasing the pulp temperature from 65°C to 90°C led to a marked increase in the percentage of oxygen

VII. Operating conditions in French mill producing softwood sulfite pulp (oxygen extraction process)

	Softwood
Pulp consistency, %	10
Caustic added, kg/metric ton	25-30
Pulp temperature, °C	60
Retention-tube pressure, kPa	
Inlet	350
Outlet	150
Retention-tube residence time, min	12.5

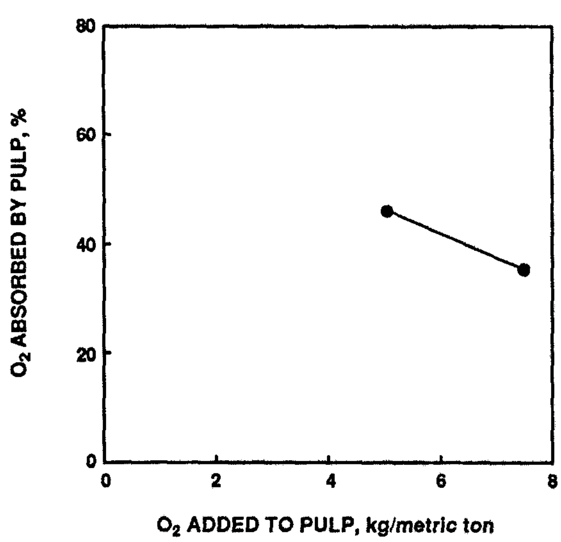
12. Oxygen content of vent gas as a function of oxygen added to pulp for French sulfite mill



VIII. Air content of pulp slurries in French mill producing softwood sulfite pulp (oxygen extraction process)

Pulp consistency, %	10
Pump	No vacuum degassing
O_2 addition	Diffuser
Air in pulp, %	7.3-10.9

13. Oxygen absorbed by pulp as a function of oxygen added to pulp for French sulfite mill



IX. Operating conditions in Swedish mill producing hardwood and softwood kraft pulps (oxygen delignification process)

	Hardwood	*Softwood*
Pulp consistency, %	7.5-8.9	6.5-8.3
Caustic added, kg/metric ton	15.0-17.4	16.1-24.3
Pulp temperature, °C	110-115	110-115
Reactor pressure, kPa		
Inlet	600	600
Outlet	450	450
Reactor residence time, min	60	60

X. Air content of pulp slurries in Swedish mill producing hardwood and softwood kraft pulps (oxygen delignification process)

	Hardwood	*Softwood*
Pulp consistency, %	7.5-9.8	6.5-8.3
Pump	No vacuum degassing	No vacuum degassing
O_2 addition	Mixer	Mixer
Air in pulp, %	5-7	10-12

absorbed by the pulp. There was a further increase in oxygen absorbed when the pressure on the outlet of the retention tube was increased from 120 kPa to 320 kPa.

3. For the medium-consistency oxygen delignification process, the tests carried out on a Swedish mill showed that both softwood and hardwood pulps consumed all of the added oxygen, along with some of the oxygen from the air entrained within the pulp slurry.
4. Pulp slurries that pass through a pump equipped with a vacuum degasser contain much less air than pulp slurries that are pumped without the degassing feature.□

XI. Oxygen absorbed by hardwood and softwood pulps (oxygen delignification process)

O_2 added to pulp, kg/metric ton	O_2 in vent gas, %	O_2 absorbed by pulp, %
	Hardwood pulps	
9.4	0-2.1	100
9.8	0.5	100
11.1	...	100
	Softwood pulps	
9.4	1.0-2.1	100
10.8	7.6-8.7	100
16.2	...	100

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