Ambient-Temperature Ammonia Removal Process for Sol-Gel Anti-Reflective Coating Solutions

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Abstract

The current sol-gel preparation process utilizes refluxing (boiling of a solution with condensation of the solvent) to remove the ammonia catalyst and halt the formation of a rigid silica-oxide network. This process requires specialized glassware, cooling water, and a controlled heat source, all of which require precise control and frequent monitoring. Removal of the ammonia by the process of bubbling a gas into the solution (purging) significantly simplifies the process and eliminates the need for a heat source. The ability to displace ammonia dissolved in 2.5 L of ethanol by purging using three inert gases (argon, helium, and nitrogen) was evaluated at a flow rate of 4 L/min in a simple setup to assess the new process efficiency versus refluxing. Similar ammonia removal rates were observed for all three gases (~24 hours to reduce the solution pH from 11 to 7). Nitrogen purging was successfully applied to remove ammonia from a 2.5 L batch of production sol-gel solution in ~42 hours with minimal effort and attention. The purging process potentially enables 2-3x more sol-gel solution to be processed in 24-43 hours compared to refluxing.

1. Introduction

Sol-gel anti-reflective coatings are used in the OMEGA EP and OMEGA laser systems at the Laboratory for Laser Energetics (LLE) to prevent beam energy losses due to reflection, known as Fresnel losses. These coatings are created from a solution of tetraethylorthosilicate (TEOS), H_2O, and ethanol. Ammonium hydroxide is then added as a basic catalyst, which increases the pH of the solution to approximately 11. Under these conditions, TEOS undergoes *hydrolysis* by OH^- ions, resulting in elimination of ethoxide radicals that are converted to additional ethanol. The remaining partially hydrolyzed orthosilicate skeleton then undergoes a *condensation* reaction, where these hydroxyl-terminated orthosilicates combine to eliminate

water and begin the formation of colloidal silica particles (Fig. 1, top) . These particles are then

aged until they reach the desired size and form a colloidal silica structure. Refluxing (boiling of a

solution with condensation of the solvent) removes the ammonia catalyst, which terminates

particle growth and decreases the pH to 7. This creates a sol-gel coating solution that can be

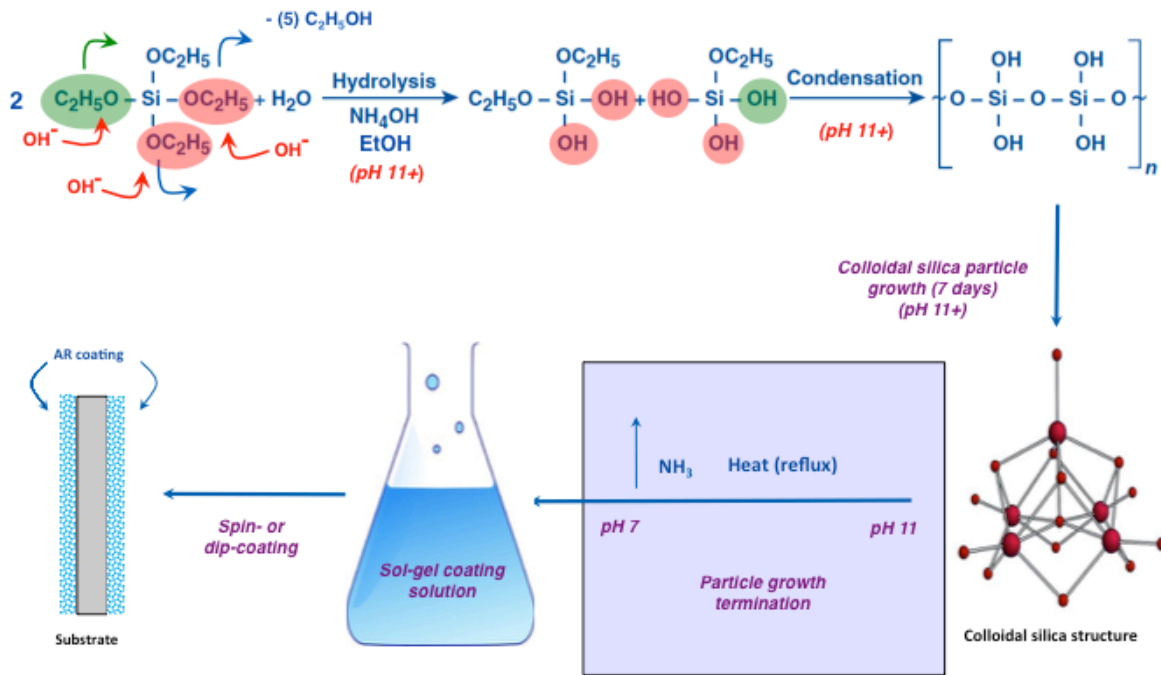spin- or dip-coated onto glass optics (Fig. 1, bottom).

Fig. 1: Formation of an anti-reflective coating via the sol-gel preparation process. Ammonium hydroxide is added as a catalyst to the solution of H_2O, ethanol, and tetraethylorthosilicate (TEOS), which initiates hydrolysis of the terminal groups followed by condensation of two or more partially-hydrolyzed siloxane chains to create colloidal silica particles of a desired size. Refluxing terminates particle growth and removes the ammonia to create a sol-gel coating solution that can be spin- or dip-coated onto glass optics.

Refluxing involves a complicated setup, which must be monitored frequently throughout

the ammonia removal process. As shown in Figure 2a, the setup includes a 5 L round-bottom

flask, a heating mantle, an electronic temperature controller, glass wool for insulation, a

magnetic stir plate with a corresponding magnetic stirrer, and a reflux-distilling head with an

integral water-cooled condenser. A steady stream of water through an inlet in the distilling head

must be maintained throughout the refluxing cycle so that condensation of the solvent (ethanol)

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can occur (Fig. 2b). The pH is measured through an outlet on the side of the distilling head (Fig. 2b). One reflux apparatus can process 2 L of sol-gel, and two reflux apparatuses can be set up at a time. Therefore, only 4 L of sol-gel can be processed within one 24-hour cycle. The Optical Manufacturing Group (OMAN) at LLE produces 20 L batches of sol-gel that have been aged to the desired particle size and transfers them in 4 L Erlenmeyer flasks to the LLE Optical Materials Laboratory. The sol-gel must then be transferred again into the 5 L round-bottom flasks of the reflux apparatuses. Overall, this process is cumbersome, and it requires 5-6 days to process a complete batch of sol-gel from OMAN.
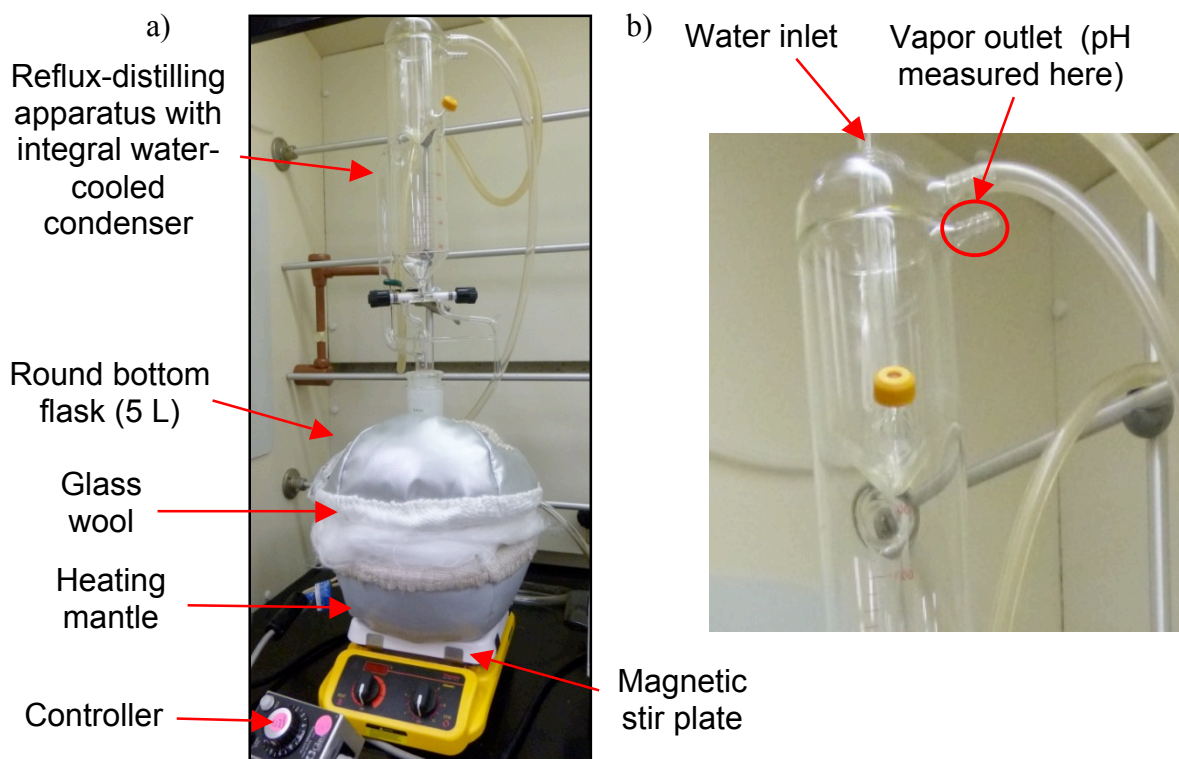

Fig. 2: Current refluxing setup. a) A complex apparatus including specialized glassware, a controlled heat source, and cooling water is necessary for refluxing. b) The distilling head includes an integral water-cooled condenser that returns the solvent (ethanol) back into the solution. The pH is measured at the vapor outlet.

In previous work, a gas purging process was developed to simplify ammonia removal and eliminate the need for a heat source [1]. The setup consists of a three-necked round-bottom flask,

an addition funnel, a magnetic stirrer, a condenser, and a gas dispersion tube with a coarse (12C) glass frit at the end (Fig. 3). Inert nitrogen gas is dispersed into the solution though the coarse glass frit to displace the ammonia within the sol-gel. The rate of ammonia loss is monitored using moistened pH paper at the vapor outlet of the condenser until a pH value of 7 is reached. The addition funnel is used to maintain the initial solution volume by adding ethanol back into the solution, while the condenser prevents too much ethanol from evaporating. This process was initially tested on a small scale with 200 mL ethanol and ammonium hydroxide solutions to determine the optimal nitrogen gas pressure and flow rate. The process was then tested with sol-gel, which yielded a similar purge time.
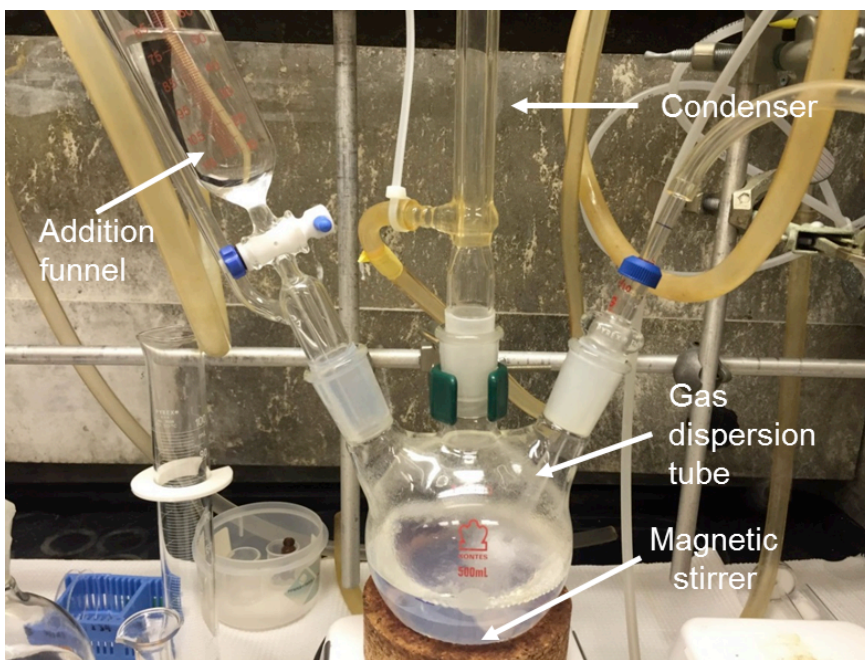

Fig. 3: Initial inert gas purging setup. A three-neck round-bottom flask was used for a small-scale prototype where nitrogen was dispersed into solution to displace the ammonia [1].

Anti-reflective coatings produced from the small-scale nitrogen-purged sol-gel solutions exhibited similar transmission and laser damage resistance to those produced by the reflux process [2][3]. At 351 nm, which is the wavelength for OMEGA and OMEGA EP, refluxed and nitrogen-purged single-sided anti-reflective coatings (non-optimized) yielded similar percent

transmittances (Fig. 4). Laser damage testing was conducted on the coatings at 351 nm using 1-on-1 and N-on-1 protocols with a 1 ns pulse width [3]. One-on-one testing involves the irradiation of different sites with single laser shots with an incremental increase in laser fluence until damage is observed, while N-on-1 testing involves the irradiation of a single site with an incremental increase in laser fluence until damage is observed. Table 1 compares the damage thresholds for refluxed and nitrogen-purged anti-reflective coatings. N-on-1 and 1-on-1 testing yielded similar laser damage resistances between the two types of AR coatings.
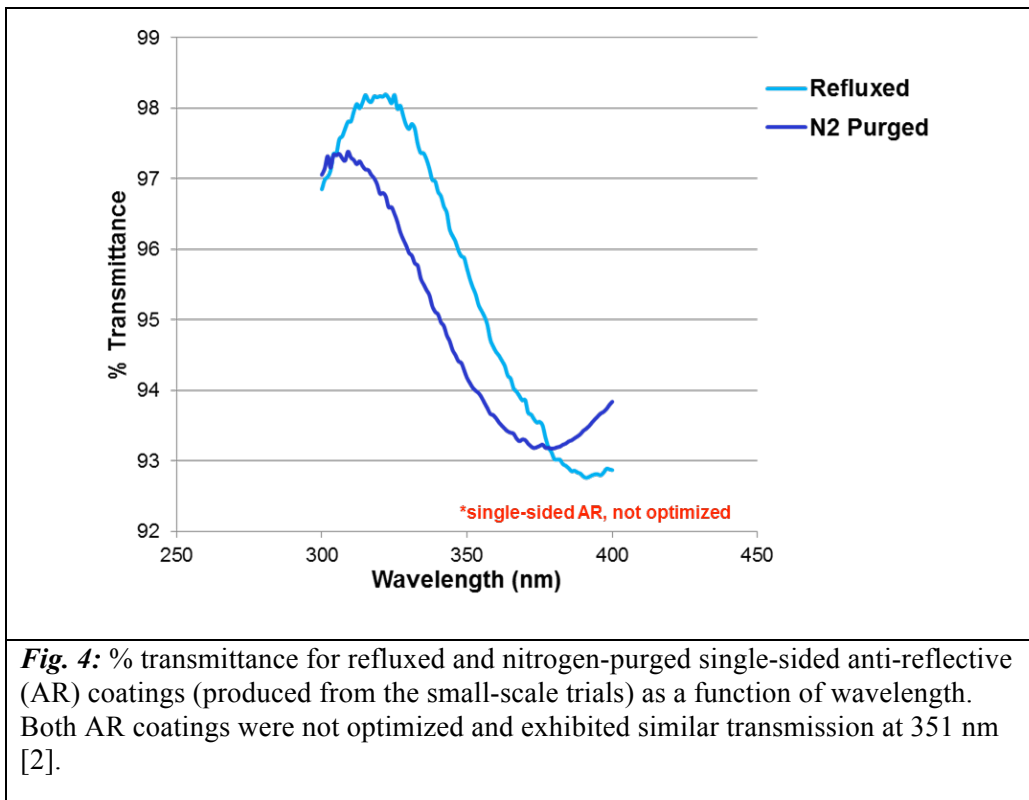

Fig. 4: % transmittance for refluxed and nitrogen-purged single-sided anti-reflective (AR) coatings (produced from the small-scale trials) as a function of wavelength. Both AR coatings were not optimized and exhibited similar transmission at 351 nm [2].

Table 1: Laser damage testing results for refluxed and N_2–purged single-sided AR coatings (produced from the small-scale trials) at 351 nm with a 1 ns pulse width [3].

Damage Testing Type	Refluxed	N_2–purged
1–on–1	8.65 ± 0.18	8.53 ± 0.09
N–on–1	15.77 ± 1.35	17.31 ± 0.40

In this work, three production scale experiments were performed in order to optimize the inert gas purging process. The first two experiments used ethanol and ammonium hydroxide solution, and the third experiment used sol-gel solution. The first experiment tested the effect of inert gas flow rate on ammonia removal time and ethanol loss. Nitrogen gas was used for the experiment, and two trials were performed: one with a flow rate of 2 L/min and one with a flow rate of 4 L/min. The second experiment assessed whether nitrogen, argon, or helium was most effective at removing ammonia from solution. A flow rate of 4 L/min was used for all three trials, and ammonia removal time and ethanol loss were recorded at the end of each trial. The third experiment demonstrated the inert gas purging process in sol-gel solution using nitrogen gas and helium gas. These experiments are vital in enabling the inert-gas purging process to replace refluxing.

2. Experimental

The inert-gas purging process was tested at production volume (2.5 L) in a simple glassware setup (Fig. 5) using ethanol and ammonium hydroxide. Rather than a three-necked round-bottom flask, a 4 L Erlenmeyer flask was used to assess the efficiency of the process with a different flask geometry. This also removes the need to transfer large solution volumes between storage vessels and the purging apparatus because sol-gel solution is generally produced in Erlenmeyer flasks. Flexible extension tubes were used to route the inert gas into the solution. The tubes were zip-tied together to prevent gas leakages. This series of tubes was then connected to a stiff extension tube, which was zip-tied to a gas dispersion tube with a coarse (12C) glass frit at the end. The stiff tube allows the frit to reach the bottom of the flask, so the gas can be evenly distributed. To maintain constant stirring at 240 rpm, a large magnetic stir bar and stir plate were used. The gas pressure was measured by a pressure gauge, and a Dwyer flowmeter with a range

of 1-10 L/min of air was used to control the gas flow rate. For the trials involving nitrogen, the gas was routed from the nitrogen source that is connected to the fume hood. For the trials involving argon and helium, the gas was routed from high-pressure gas cylinders through two-stage gas regulators, which were used to set the argon and helium gas delivery pressures. Three experiments were performed: the first testing the optimal flow rate, the second testing whether nitrogen, argon, or helium had the most efficient ammonia removal rate, and the third testing inert gas purging in sol-gel solution.
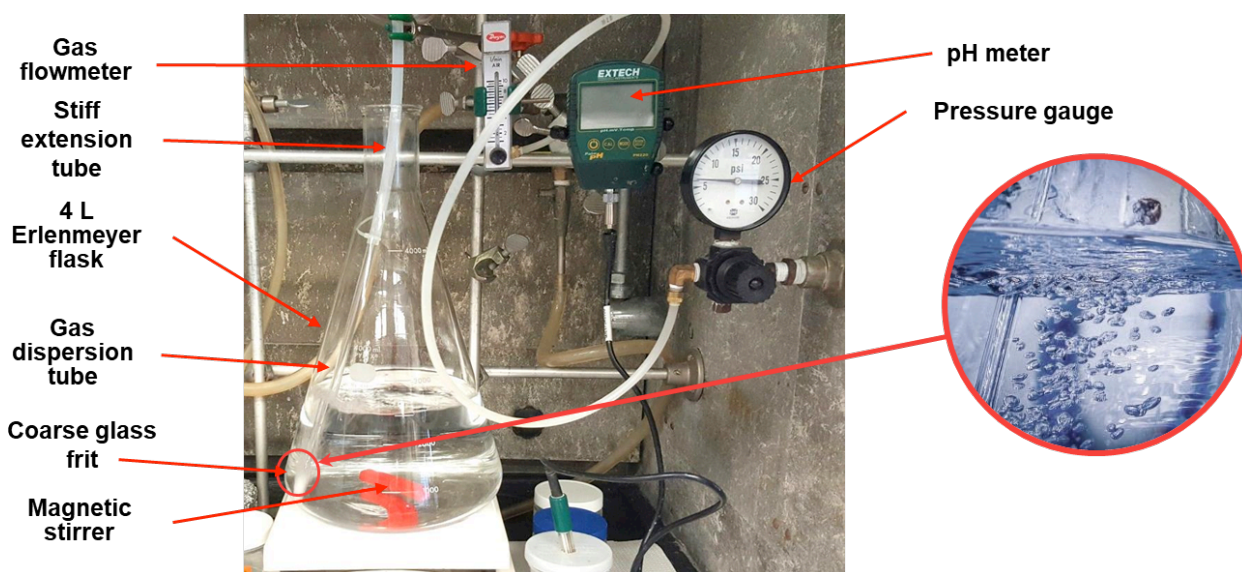

Fig. 5: Production-scale gas purging setup with a solution of ammonium hydroxide and ethanol. Gas is dispersed into solution by a coarse glass frit that creates bubbles that help displace the ammonia gas. This figure shows the purging setup used for nitrogen.

2.1 Effect of flow rate

The first two production-scale trials were performed with nitrogen gas at flow rates of 2 L/min and 4 L/min. Since nitrogen makes up the majority of air, it was treated as air when setting the flow rates with the Dwyer flowmeter. Ethanol (2430 mL) and ammonium hydroxide (70 mL) were used in both trials. The gas pressure was set so the pressure gauge inside the fume hood read 7 psi, before turning the flow meter on. A line was marked on the outside of the flask to indicate the initial solution level before purging was started. No measures were taken to prevent

ethanol loss (no condenser was used), and ethanol was added using a graduated cylinder at regular time intervals to maintain the initial solution volume. The pH was measured from an inch below the opening of the flask with both a pH meter and pH paper. There seemed to be a disparity between the values shown by the pH meter and the pH paper, possibly due to a slight calibration error in the pH meter. The pH paper seemed to more accurately measure the rate of ammonia loss, but since it measures only in integer values, the pH meter values were used for graphing the results to show the rate of ammonia loss. Each trial was stopped once a pH of 7 was reached according to the pH paper.

2.2 Choice of inert gas

Other inert gases were evaluated for their ability to remove ammonia from sol-gel solution. Solubility and viscosity properties of three gases were compared to that of ammonia to hypothesize which gas would be the most viable candidate. Argon and nitrogen gas both have a high solubility in comparison to ammonia, which indicates that they would displace the ammonia catalyst more readily than those with a lower solubility (Table 2). Nitrogen seemed to be the most viable candidate because of its high solubility and moderate viscosity. Although helium gas has a lower solubility, this property would make it the easiest to remove from solution, which is why the gas was still tested in the production-scale experiments.

Gas	Solubility in Ethanol (cm³/kg)	Viscosity (10⁻⁵ Pa*s)
He	38.4	1.96
Ar	309.7	2.23
N_2	393.7	1.76
NH_3	87.8	0.99

Table 2: Solubility in ethanol and viscosity for helium, argon, and nitrogen in comparison to ammonia [4][5]. These inert gases were evaluated for their ability to remove ammonia from sol-gel solution based on their chemical properties.

Nitrogen, helium, and argon were used for purging tests in ethanol and ammonium hydroxide solution. Ethanol (2430 mL) and ammonium hydroxide (70 mL) were used for all three trials. The desired flow rate for each gas was 4 L/min, but since the Dwyer flowmeter measures the flow rate of air, a correction factor was applied to calibrate the gas flow rates in terms of air. The correction factor was multiplied by the desired flow rate (4 L/min) to get the air equivalent [6]. Argon's correction factor is 1.18 [6], which yielded a flow rate of 4.72 L/min of air. The gas regulator was set to approximately 2.1 psi for the argon trial. For helium, the correction factor is 0.37 [6], which yielded a flow rate of 1.48 L/min of air. The gas regulator was once again set to 2.1 psi for the helium trial.

2.3 Application to sol-gel solution

The purging process was applied to a 2.5 L previously made sol-gel batch using nitrogen at a 4 L/min flow rate. Since the ammonia catalyst had already been removed from this sol-gel, 72 mL of ammonium hydroxide was added to the 2.5 L of sol-gel. The nitrogen pressure was once again set to 7 psi. Helium was also tested using a 2.5 L sol-gel batch and 72 mL of ammonium hydroxide at the calibrated flow rate for helium, and the pressure was set to 2.1 psi.

3. Results and Discussion

3.1 Effect of flow rate

Figure 6a illustrates the effect of gas flow rate on ammonia removal time in ethanol and ammonium hydroxide solution for nitrogen gas. When the flow rate was doubled from 2 L/min to 4 L/min, the purge time was cut approximately in half, from 43.5 hours to 23 hours.
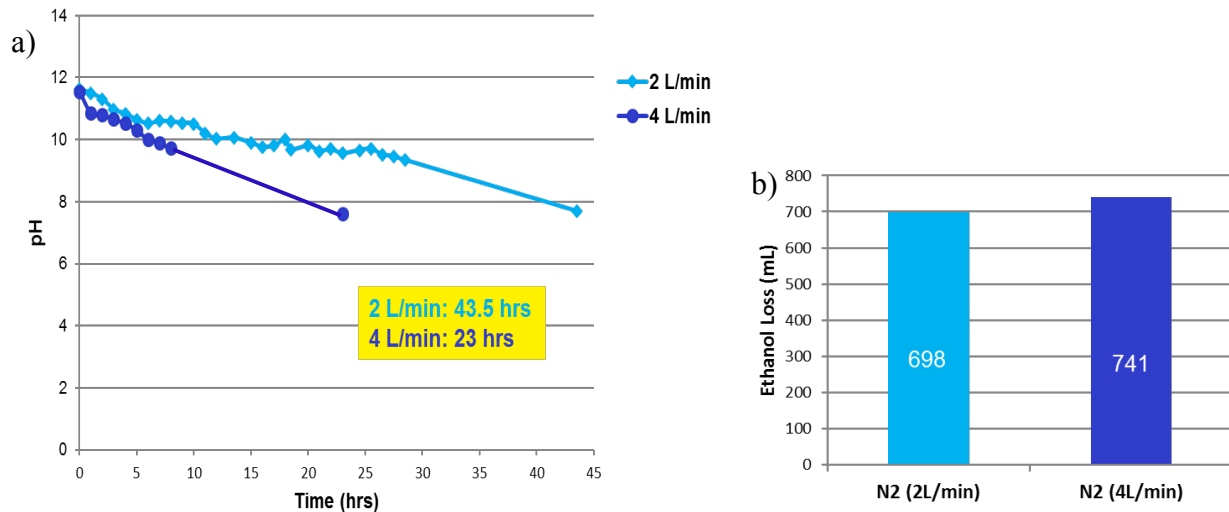
Fig. 6: a) pH as a function of time for nitrogen purging in ethanol and ammonium hydroxide solution at 2 L/min and 4 L/min. Doubling the flow rate cut the ammonia removal time in half. b) Total ethanol loss for nitrogen purging at 2 L/min and 4 L/min. The ethanol loss was not significantly affected when the flow rate was doubled.

The ethanol loss for the 2 L/min trial was 698 mL (27.9% loss), while the loss for the 4 L/min trial was 741 mL (29.6%) (Fig. 6b). This is not a significant difference, which indicates that 4 L/min is a more optimal flow rate than 2 L/min.

3.2 Choice of inert gas

Nitrogen, helium, and argon performed similarly in removing ammonia from the ethanol solution at a gas flow rate of 4 L/min. There was no significant difference between the purge times of the three gases, as the data only ranged from 23-26.5 hours (Fig. 7a). In terms of ethanol loss, argon performed better than the other two gases, with an ethanol loss of 532 mL (20.9%), compared to 741 mL (29.6%) for nitrogen and 664 mL (26.6%) for helium (Fig. 7b). The cause for the differences in ethanol loss seems to follow the patterns illustrated by the gases' viscosity properties. Argon has the highest viscosity at 2.23 [5] and the least ethanol loss, while nitrogen has the lowest viscosity at 1.76 [5] and the greatest ethanol loss. However, the ethanol loss results do not correlate with the solubility data for each gas. More trials will have to be performed to confirm whether argon has significantly lower ethanol loss.
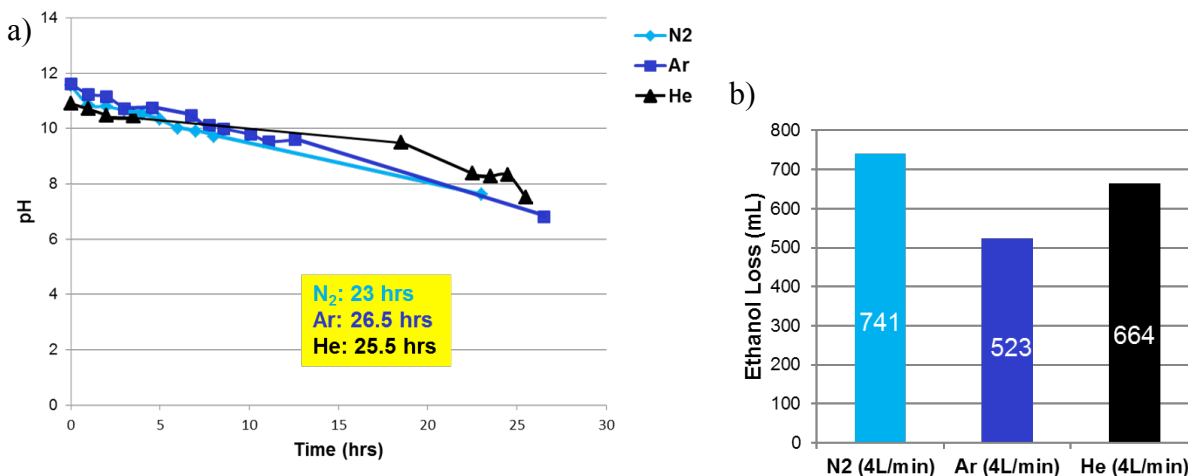
Fig. 7: a) pH as a function of time for nitrogen, argon, and helium purging in ethanol and ammonium hydroxide solution at 4 L/min. All three gases had similar ammonia removal rates. b) Ethanol loss for nitrogen, argon, and helium purging at 4 L/min. Argon had the least ethanol loss even with the greatest ammonia removal time.

3.3 Application to sol-gel solution

Conditions were controlled so that the nitrogen and helium purging trials with sol-gel batches could be compared to the trials with ethanol and ammonium hydroxide solutions. Helium took longer than nitrogen, with complete ammonia removal occurring after 47.8 hours in comparison to 42.75 hours (Fig. 8). However, helium's ethanol loss was less than nitrogen's, only 35.6% compared to 44.3% (Fig. 8). For both nitrogen and helium, the purge times for the sol-gel solutions were almost double those for the ethanol and ammonium hydroxide solutions. This is most likely because ammonia became trapped in the porous structure of sol-gel, making it harder to purge out. The ethanol loss was also greater for both sol-gel trials, because their purge times were two times longer.
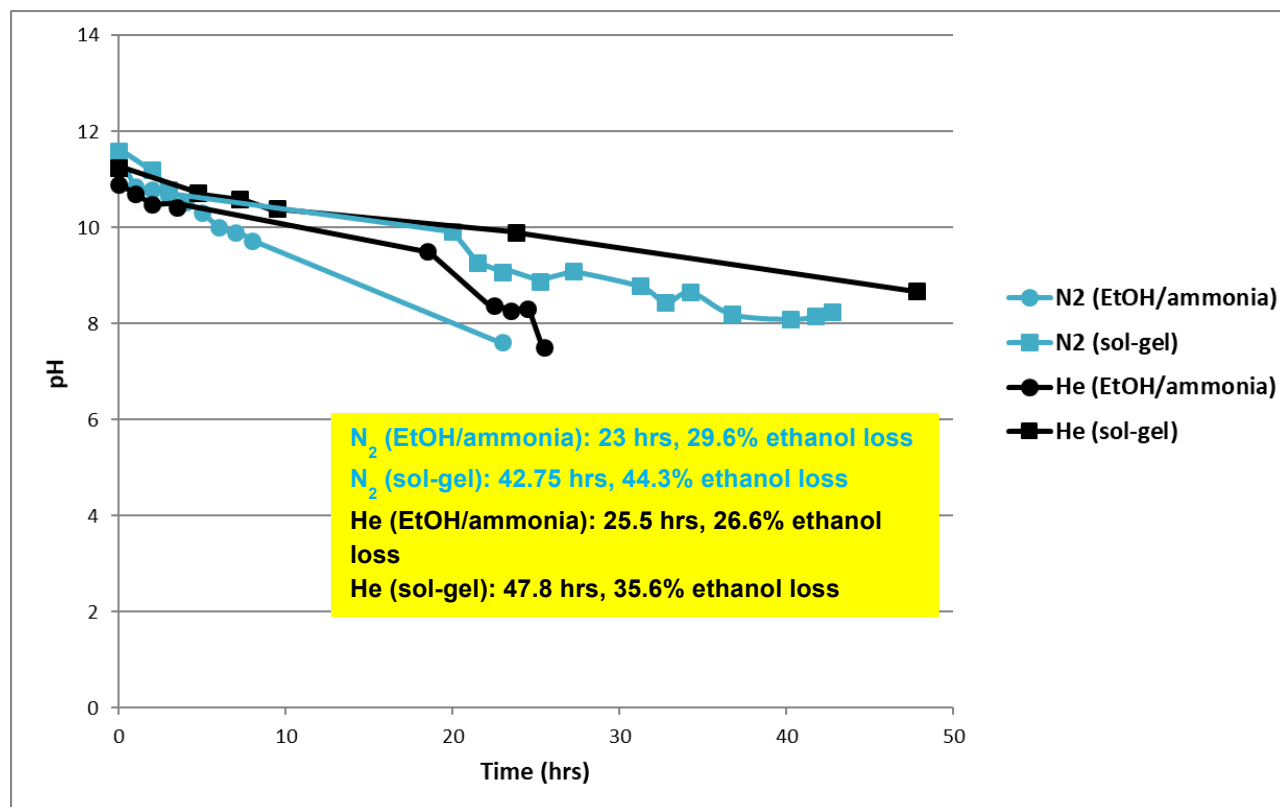
Fig. 8: Nitrogen and helium purging in a solution of ethanol and ammonium hydroxide compared to purging in sol-gel. The ammonia removal time doubled for purging in sol-gel for both gases.

4. Conclusions

A simplified inert-gas purging setup streamlines ammonia removal for sol-gel coating solutions. Nitrogen, helium, and argon were tested to see if one inert gas would outperform the others, but all three gases had similar purge times. Nitrogen is generally the most abundant gas in laboratories and is the easiest to handle, therefore making it the most convenient and lowest-cost option. The inert-gas purging process can be successfully applied to production-scale sol-gel batches using nitrogen gas at a purge rate of 4 L/min. As a result of the simplicity of the inert-gas purging setup, 4-5 apparatuses can be setup in one fume hood. Using refluxing, only 2 apparatuses can be set up within one fume hood. Inert-gas purging requires little equipment compared to refluxing and can process 2.5 L of sol-gel per setup. Therefore, this new process

would allow for 2-3x the volume of sol-gel solution to be processed in 24-43 hours with significantly less effort than by refluxing.

5. Future Work

Additional studies remain before the gas purging process can be validated for sol-gel coating production. Further trials should be conducted using condensers with closed-loop, Freon-based refrigeration cooling to minimize solvent loss. Although ethanol will still have to be added to maintain the original solution volume, resource costs will be reduced if a more efficient setup is created. Any other alterations to the design that can increase the efficiency of the process should be analyzed. Different glass frit porosities, such as an extra-coarse frit, could decrease the ammonia removal time at a given flow rate. Alternative flask geometries could have an effect on the purge rate or the distribution of the inert gas in the solution. Laser damage testing and AR coating quality testing should be determined for a gas-purged, production-scale sol-gel coating batch to be compared to the small-scale trial damage thresholds obtained from previous work. The sol-gel coating batch will likely be purged with nitrogen gas, because helium and argon did not perform significantly better in the trials. The resulting solution will be dip-coated onto a glass optic for testing. If the laser damage threshold is high enough, a production-scale, nitrogen-purged sol-gel AR coated optic should be tested on OMEGA.

6. Acknowledgements

regarding refluxing. Finally, I thank all of the Materials Lab staff and students for being so welcoming and making my experience enriching and enjoyable.

7. References

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