Precautions for Ammonia Storage Tanks

In the event of a leak, a high dike surrounding an ammonia storage tank can keep evaporation to a minimum, and protect the tank in case of a nearby explosion.

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In 1967, the Ammonia Storage Committee made an interim report to the AIChE Ammonia Plant Safety Symposium. This report stated in part: "Concerning large spills of liquid ammonia, dangerous ammonia vapor concentrations could be expected at relatively long distances if the liquid were allowed to spread, especially during adverse weather conditions such as thermal inversion combined with low wind velocity."

This statement should make us all more conscious of the need for safety in ammonia storage. What it says is that a large ammonia spill is not just a plant safety problem, it is a community safety problem. We must do everything we can to avoid a large ammonia spill, especially in densely populated areas. As a minimum, we should observe what might be called the Basic Safety Precautions for ammonia storage facilities.

Basic safety precautions

1. All vessels and piping designed and constructed in accordance with applicable codes. (Many hours of engineering time have gone into the piping and vessel codes to insure against failure. We must observe these codes or improve on them if possible.)
2. Alarms or trips to minimize the opening of pressure or vacuum relief valves. (Pressure or vacuum relief valves can stick in the open position. Alarms or trips should limit their use as much as possible.)
3. Remove shut-off, excess flow, or check valves on all large liquid lines. (The most probable cause of a major spill is a hose or piping failure. The piping is subject to physical damage by moving vehicles, especially in loading operations. There should be provision to automatically or remotely shut off the flow in case of a large piping leak.)
4. Minimum and careful use of small connections. (Small connections are the most subject to failure. Even though the leak size will be small, minimum and careful use of small connections should be observed.)
5. Full-sized dike around tanks. (It will be shown later that a normal full-sized dike is not much protection during unfavorable weather conditions, but it is certainly preferred over allowing a tank leak to spread indiscriminately. The dike also provides a barrier against vehicle access to the tank.)
6. Well trained operators. (Everyone knows that well trained operators are a must when handling potentially hazardous materials.)

These six Basic Safety Precautions should prevent a major spill, and so far the experience has been good. However, in spite of the good record, we cannot help but be concerned about the possiblity of a large leak in the storage tank itself. The potential consequences are such that we must be concerned about the possiblity. Some of the causes of storage tank leaks are noted below:

1. Tank penetration by a missile or fragment from a nearby explosion. (Sabotage must be considered in addition to accidental explosions.)
2. Faulty material or construction. (In spite of the codes.)
3. Corrosion (either internal or external).
4. Stresses caused by expansion or contraction.
5. Stresses caused by foundation failure, especially in atmospheric pressure tanks where frost heave is a possibility.

All of these possible causes may not be realistic, but we are sure that some of them are, and we are also sure that the list is not complete.

The fact that concerns me is that the usual dike around the tank is not adequate protection against a large storage tank leak. The 1969 report of the Ammonia Storage Committee indicated that with an atmospheric inversion and low wind velocity, a 1,000 ppm ammonia concentration could exist at a distance of 30 pool diameters from the spill. What does 30 pool diameters mean for a typical storage tank dike?

Figure 1 shows a dike 8 ft. high and 470 ft. square surrounding a 30,000 ton storage tank. Thirty pool diameters is approximately 2-1/2 mi. In other words, if the dike is full of ammonia when there is an unfavorable weather condition, a concentration of 1,000 ppm could be present at a distance of approximately 2-1/2 mi. Lower, but still hazardous, concentrations could be present at much

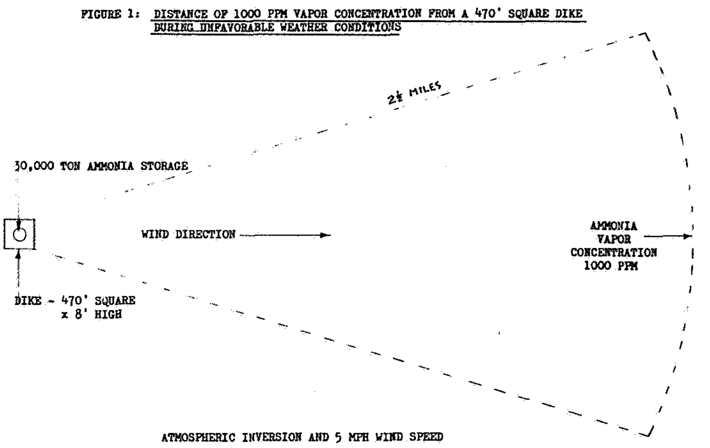

Figure 1. Distance of 1,000 ppm vapor concentrations from a 470 ft. sq. dike during unfavorable weather conditions.

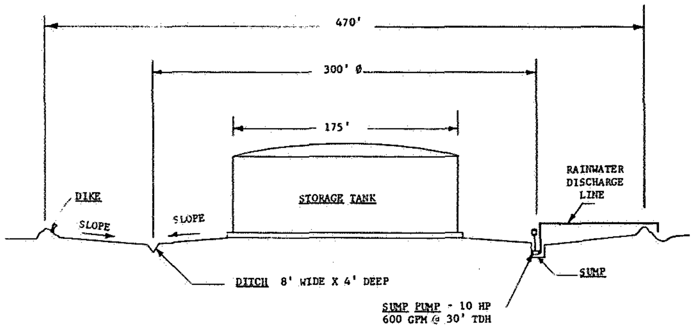

Figure 2. A method for limiting ammonia spill area through controlled drainage.

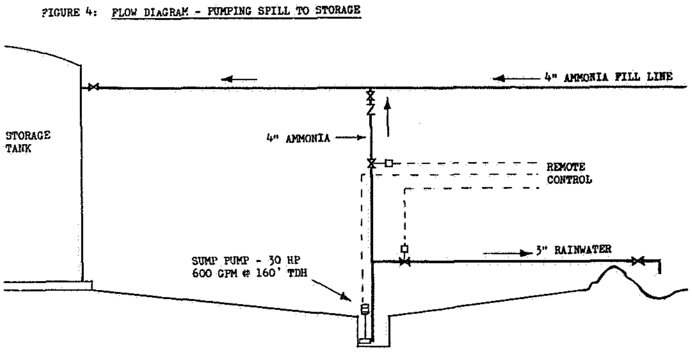

Figure 3. Flow diagram showing a technique for pumping ammonia spill to storage.

greater distances.

At first glance one might think that the possibility of a storage tank failure, and an unfavorable weather condition at the same time, is very remote. However, the Ammonia Storage Committee report also indicated a steady-state evaporation rate of 140-to 220 ton/hr. for this dike size. At these rates it would take 6- to 8 days to evaporate 30,000 tons. During this length of time, an unfavorable weather condition would be quite probable. In view of these data, it seems that we are not justified in feeling safe just because our tank is surrounded by a large dike. Clearly, some additional safety precautions should be considered.

Stronger dike designs

Some companies have obtained excellent protection by installing a dike as tall as the tank. These dikes have been built of either steel or concrete at a cost of about $500,000 for a 30,000 ton tank. This cost is substantial, but it certainly should be considered in densely populated areas. The high dike will not only keep the spill evaporation to minimum, but it gives protection to the tank in case of a nearby explosion.

If you cannot justify a dike as tall as the tank, some other method of keeping the spill area to a minimum should be found. Figure 2 shows one such method. The floor of the main dike is sloped to a ditch 8 ft. wide and 4 ft. deep. A sump pump removes the rain water from the ditch to the outside of the main dike. The ditch shown has a surface area of 7,500 sq. ft. when full, and even less when it is not full. This compares to a surface area of 200,000 sq. ft. for the main dike. The distance of a given concentration due to a steady-state evaporation from this ditch will only be about one-fifth of that from the main dike. For low wind velocity and atmospheric inversion, the distance of the 1,000 ppm concentration will be approximately one-half mile instead of 2-1/2 miles from the tank. Of course, unless the leak can be stopped, the ditch will eventually be filled. However, the ditch shown will hold about 120,000 gal. In case of a 1,000 gal./min. leak, it would take more than 2 hr. to fill the ditch, which would give some time for an orderly evacuation. The sump pump could also be used to pump the spilled ammonia to any available tank cars or trucks. The cost of this ditch, complete with sump and sump pump, should be approximately $10,000.

A logical extension of this scheme is to provide a high head pump and a discharge line to the storage tank. Figure 3 shows one potential design. The pump can discharge rain water to the outside of the main dike, or it can discharge an ammonia spill back into the storage tank. The pump and discharge valves are operated remotely. If the leak is smaller than the pump capacity, the ditch will not overflow. The existing load-out facilities can be used to empty the tank for repairs.

On an existing tank, the maximum practical pump capacity will probably be determined by the size of the existing fill-line. With a 4 in. dia. fill-line, a pump with a capacity of about 600 gal./min. can be installed. This pump would require approximately 30 h.p. and the entire installation (ditch, sump, pump, piping, motor, electrical switch gear and remote controls) would cost approximately $20,000 installed. With an even larger fill-line, higher pump capacity can be installed without excessive cost. The cost/benefit ratio of this scheme seems extremely attractive.

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An idea which deserves further study is the blanketing of the ammonia liquid with some kind of foam or pellet to reduce the evaporation rate. Research should be undertaken to determine the effect of the heat input by the foam or pellet, the overall effectiveness of this procedure, and its cost.

Precautions to avoid

I have also considered some other possible safety precautions, but have not found them especially attractive. The use of water sprays on the vapors from a large spill does not appear reasonable. As noted earlier, the evaporation rate from a 470 ft. sq. dike would be 140- to 220 ton/hr. To make even a 10% solution would require about 8,000 gal./min. of water, and disposing of 8,000 gal./min. of 10% aqua may be an even greater problem.

To use water directly on the liquid spill would only increase the evaporation rate. This should be done only if the spill is small and the weather conditions are favorable for atmospheric dispersion.

Burning of the vapors from a spill does not seem practical either. The lower flammable limit of ammonia is so high that concentrations in the flammable range will not normally be encountered without forced evaporation. A sump with an evaporator and a flare might be possible, but the pump approach seems to be more practical. #

COMEAU, E. T.

DISCUSSION

Q. Do any of those numbers you used in your research relate to the Phillips experiment at Bartlesville. I believe you said there was a dike full which evaporated empty in 2-3 days. This kind of scares me; is this what I heard, or did I misunderstand you.?

COMEAU: If the dikes were full and at a steady state evaporation rate, it would take six to eight days to evaporate 30,000 tons. Of course the tank may not be full and the initial evaporation rate will be higher. If you started with a large leak from a full tank, it would probably be five or six days before all the ammonia evaporated.

In regard to the Phillips paper, I can say that the Ammonia Storage Committee did review the Phillips work in detail, and generally it does correlate with the other work done by the Ammonia Storage Committee, And it ought to be noted, that the Phillips spill test was made under ideal weather conditions. The numbers I gave on concentration distances are with atmospheric inversion and low wind velocities, very similar to the conditions at the Blair spill.

Under conditions where you have a lapse state (the opposite of an inversion), and high wind velocity, the problem is diminished by a very large factor. You are fortunate if you have those conditions when you have a major spill.

G.M. CAMERON, Canadian Industries, Ltd.: I'm sorry if my experience here perhaps is not the same as yours, and perhaps I should ask a question or two. From our experience in storage of material such as ammonia, SO_2 in this specific case, we found that the basic rate of evaporation is probably more likely related to the heat capacity of the soil, rock, or whatever it happens to be that your ammonia is in. And in this respect, stopping the source of the heat which causes the evaporation probably of your liquid is likely going to be more significant than dike at our Pernis works, but at our Jimuiden works, where the tank is located at the site of a steel works, we did build a prestressed concrete wall of the full height around the tank. It is a 10,000 tons tank and the extra civil cost for the concrete wall amounted to $100,000.-.

All other costs remained about the same.

COMEAU: It should be pointed out that the high dike price given in the paper was for a 30,000 ton tank. The dike cost would probably be linear with tank size. On this basis the cost for a high dike around a 30,000 ton tank would be $300,000 instead of $500,000 to $700,000.

HAYS MAYO, Cooperative Farm Chemicals Assn.: I think that some savings could be made by using a safety factor lower than four to one. A safety factor of two to one would seem adequate for this type of installation.

M.W. ESCHENBRENNER, Kellogg Co.: I don't consider it correct to state that any tank has a four to one safety factor. Such a factor is measured against ultimate failure. However, yielding occurs at a much lower stress level and any factor against yielding is less than 1.5.

ANON: In the Blair incident paper, I believe it was 160 ton of ammonia spilled, and it created a vapor cloud of 9,000 ft. That represents only 1/2% of the quantity in the large storage tank. I wonder whether any scheme that required any operational procedure would really have any chance of working in such a situation, because I can envision that if it's not there, I just wonder what could be done.

COMEAU: At the Blair spill, water was used to increase the evaporation rate. The downwind concentrations obtained from this high evaporation rate (160 tons in 2-1/2 hours) correlate very well with the Ammonia Storage Committee data for the weather conditions at Blair (inversion and low wind velocity). This incident confirms my belief in the use of minimum surface area to control the evaporation rate.

trying to prevent it evaporating at the surface because in due course ammonia in a pool is going to chill everything below.

Now I wonder if there is any comment on thermal barriers with the soil below instead of from the air?

COMEAU: My memory is not too good on this point, but as I recall, very little of the steady state evaporation rate was caused by heat from the soil. The soil would freeze rapidly and form an insulation barrier. The major steady state factors are radiation and convection to the air. The initial evaporation rates are considerably higher until the ground is cooled down.

During this time, the buoyancy of the ammonia vapors is also higher because the stream is more concentrated. The work of the Ammonia Storage Committee showed that because of the buoyancy effect, the concentrations at a distance were not significantly different from the concentrations caused by the steady state evaporation rate. One more comment. The price given for the high dike is very rough. We tried to get some accurate numbers but were unable to do so. We think that ICI has a concrete dike and we think it cost quite a bit less than the amount given in the paper.

JOHN M. BLANKEN, VKF-Mekog-Albatros, Holland: We have a normal double wall type storage tank with a low

W.H. DOYLE, Factory Insurance Assn.: I don't want to speak specifically to ammonia but more to the problem of low temperature storage of hazardous materials. The NFPA committee, at its meeting in May in Sanfrancisco, approved a new standard on liquefied natural gas. The basic philosophy in that standard is, I think, the same. You will not ordinarily have a spill larger than that caused by the failure of the largest connection below the liquid level.

We do not believe you can engineer against a total failure of a tank. That's one. Item two, the high dike concept is the most valid except that we believe that the dike should be of earth and sloped. If any of you have landed in Newark you may have seen the LNG tank on Staten Island which is a reenforced concrete tank with a liner, and with earth mounted up completely around it so it looks like an artificial hill.

That tank will survive, or the dike around it will survive, a plane impact and gas will not be released. If a plane does the impossible and dives into the top of the tank, the only surface exposed will be that of the cryogenic liquid, and there will be no heat input except from the atmosphere and that is relatively low.

I think one should not be the high dike but the high dike reinforced with earth, and the second concept should be your high dike.

DISCUSSION

Q. Were the cracks in all cases transgranular, or was it a combination of intergranular and transgranular as far as the stress corrosion cracks in places?

LIVINGSTONE: That's the sort of question that I think is best answered by Dr. Clark, one of our metallurgists who is present.

W.D. CLARK, ICI Billingham: The microstructure was confused, but some of the cracks clearly followed the prior austenitic grain boundaries while others were transgranular. The only likely cause of such cracking is stress corrosion, perhaps with hydrogen embrittlement.

FRED JONES, Chemetics, Montreal: As a representative of one of the companies that suffers this phenomenon, I'd like to point out how remarkably rapidly it can proceed. We had a rotor failure about August 15, 1967, by this mechanism. There was a synthesis gas fire in the area due to damaged seals and escaping gas.

We replaced the rotor, accepting the assurance of the manufacturer that we had foreign objects such as nuts and bolts go through the machine. We were somehwat incredulous at this but deferred to expertise in this area. The new rotor I believe ran something less than 20 days before it failed in precisely the same manner. We were sure that there were no foreign bodies in the machine on the second failure.

We have lost the record since then. Someone else suffered a rotor failure in less time than that. Stress corrosion cracking appears to be able to proceed very rapidly, at least with a clean rotor, and is not a long term effect if carbamate has free access to the cold worked rivet head.

LIVINGSTONE: Certainly the number one plant. I mentioned two failures—the last two failures were on the one plant. The second failures was only a matter of days behind the first one.

W.E. ELLIS, Du Pont Co.: At the time I remember this examination you found cracks only in the cold worked portion of the rivet head. Is that correct, Willie?

CLARK: Yes, that is correct.

ELLIS: Under these conditions we took one additional step with the epoxy treatment. We inverted the rivet and put the head on the cover side of the wheel and did all the cold working of the rivet on the back side of the disc so that the cold worked portion would be less likely to see the carbamate.

LIVINGSTONE: One point I'd like to make, I meant to make during the talk; I don't know whether I did. And that is that looking at the thermodynamics of the formation of carbamate and its dissociation constant, it is not or should not be stable under ambient conditions, and yet we have found substantial quantities of carbamate probably stabilised by oil, existing for days under these conditions.

JAYS MAYO, Cooperative Farm Chemicals Assn: How did you alter water concentrations in the methanator?

LIVINGSTONE: We removed the - or dropped the water inlet concentration by bypassing the semilean vetrocoke exchanger in fact. In doing this, we raised the semilean temperature but dropped the lean temperature at the top of the absorbers, and in fact we gained in CO_2 removal performance. I mentioned the absorber top temperature on the number one plant, about 108 degrees, and the other two running at 70. We got as low as 85 on the number one plant just by bypassing this exchanger. And in fact, while I am here, almost certainly be in the throes of online cleaning one half of the remaining exchanger to drop that temperature even further.

So this is the way we managed to keep it down. Whether or not the catalyst manufacturers would like to say anything about the water business I don't know. The one thing that is bothering me at the moment, and this is why we've gone to a sidestream methanator to try and inject water and see what is happening, is that these effects are not in line with the expected drops that you would get from thermodynamic data.

JOHN S. CROMEANS, Catalyst Consulting Services, Inc.: We know that water is an inhibitor on the methanation catalyst. In the design of methanators following systems which have a high temperature leaving the CO_2 solvent removal - such as hot potassium carbonate or other type solutions - where one will have a higher water vapor content, it is advantageous to provide methanators which are significantly larger and/or use higher activity catalysts.

We also know that the rate of hydrogenation of CO_2 is much slower than the rate of hydrogenation of CO, generally on the order of one half of the rate for the hydrogenation of CO_2 compared to CO. We do not have precise knowledge of the kinetic effect which he referred to. But we do know there is an effect on activating the catalyst and there's an effect in operation. But the data published are not real precise. If Phil Ruziska is here from Esso, he could give us some data on the highest concentrations of water that are operating commercially.

P.A. RUZISKA, Esso Research & Engineering: We have a plant operating with about 7% water in the feed. The first three charges of methanation catalyst we tried started off at abnormally low activity and deteriorated rapidly. Two different brands of catalyst were involved. The fourth charge, of a third brand of methanation catalyst, is doing much better. It also demonstrates a lower level of activity than we would get with 1-2% water content, but the activity has not deteriorated rapidly as did the previous charges.

J.M. BLANKEN, V.K.F. Mekog-Albatros, Netherlands: The ammonia plant at Pernis of Ammoniak Unie N.V., which we operate, has a synthesis loop with single separation of ammonia, as - as I understand - most of the U.S. ammonia plants have. This means that the ammonia concentration of the gas in the recycle wheel of the synthesis gas compressor is about 10%. In November 1967 we nearly lost the rotor of the high-pressure case of our syn-gas machine.

With the plant operating at design capacity we had to increase the speed of the syn-gas compressor and at a certain stage we could not make design production anymore, because of the compressor. We opened up the machine and found carbamate in the first rotor wheel of the high pressure case. We checked according to the carbamate equilibria given in Industrial and Engineering Chemistry whether we could have made carbamate and found that with 5 ppm of carbon dioxide and 3,000 ppm of ammonia at about 65 kg/cm^2 gauge and 8°C you can make carbamate and that was apparently what we had done.

After the incident we calculated the allowable carbon dioxide concentrations for different ammonia concentrations and worked according to these.

One other comment I should like to make. For other reasons we measure the quantity of gas leaking through the labyrinths of the balance piston of the high pressure case both at Pernis and at IJmuiden. Now we find in both plants that the leakage is about 5,000 Nm^3/h.

So whereas one is inclined to think that there is hardly any ammonia in the suction of the compressor, the leakage along the balance piston alone brings 5,000 Nm^3/h gas containing 10% of ammonia in the suction resulting in an ammonia concentration of roughly 5,000 ppm. This ammonia concentration already corresponds to a maximum allowable carbon dioxide concentration of 0.5 ppm at 7°C and 63 kg/cm^2/ gauge.

Now with these figures in mind we operated for the last one and a half year with an inlet temperature of the high pressure case of 18°C instead of the design 8°C.

For those interested: We calculated the following maximum allowable carbon dioxide concentrations at different ammonia concentrations and temperatures.

Pressure 63 kg/cm^2 gauge

Ammonia concentration ppm (vol.)	**Temp. °C** 7	10	13
1,000	14	30	60
3,000	1.5	3	6.5
5,000	0.5	1.1	2.4
10,000	0.13	0.28	0.6

max. CO_2 ppm (vol.)

These values are based on the information in Industrial Engineering Chemistry and I understand from Dr. Livingstone that the new I.C.I. figures are slightly different. But we work according to these and we have had no problem.

LIVINGSTONE: That is correct. The reason we went in fact to laboratory experiments to check .around the working pressures here was that looking at the graph that I've referenced in the paper. they collected the association constant data from pretty well all the workers in the field and the scatter that starts to occur as you move up to 45°C is getting a little bit beyond creditability to extrapolate that straight

JONES: I'd like to draw your attention to the fact that all of these failures have been inlet wheels, and in our view this almost certainly is due to the fact that this is the only wheel in which water or a fluid would be likely to exist. In later stages one would expect the system to be above the dew point of any of the fluids that may be present and non-corrosive. I though we might go on to a consideration of the welded wheel construction.

I'd like to ask Willie Clark, as the expert, if he might clear something up for me and perhaps a few others. In the industry there is a standard of hardness which is appropriate for sour gas operation. I believe that this is reported as being in the region of 220 Brinnell in relation to weldments or quenched and tempered materials and the like.

It would be perhaps preferable for this inlet wheel to be held to that hardness range; that is from the point of view of the quenched and tempered material and the weldment which is made.

LOU CASERTA, American Oil Co.: We had somewhat similar failures on an air compressor in our No. 2 plant which were riveted wheels. The second rotor lasted a bit longer than the first. We have replaced them with welded wheel construction and have returned to maximum rated speeds. We had limited speed while we had the riveted wheels in. The redesigned wheels have been in service for fewer hours than the first two failures, but we have hopes that they'll continue to give us good performance indefinitely.

I have one or two questions I would like to ask. On CO_2 concentrations in methanation effluent gas, have you had any difficulty in analyzing CO_2 in these low levels? Do you do it with perhaps continuous analyzers, or are they spot samples? And the second question is if you have the ability to explore increasing methanator inlet temperatures, have you done this any and does it do any good?

LIVINGSTONE: Well, the answer to the first one is that I don't think it was a difficulty in analyzing for CO_2 with the earlier infrared instruments. The problem there was that the range of instrument was for covering a design spec of less than ten parts per million concentration. The range of instrument was for 0.50. And when you see you're running as close as you are there to deposition limits, then you want something a little more accurate, and it was really the accuracy rather than any question of difficulty analyzing, and in putting in — we went to a Hartman and Braun instrument. It is a British instrument that has been developed and we worked with them to develop this thing a bit further, to get a much longer optical bench and get an accurate determination of the CO_2 alone, and this is where we've got to at the moment.

On the second question, that one really hurts, because the inlet methanator temperature design is 315 degrees centigrade and I live to see the day when we get it there. We can't operate anything above 285-286. But it is something we are looking into at the moment. We can do about this - we have after the LT shift before the methanated preheaters — a waste heat boiler raising 50 pounds steam, low grade steam, and I think that the best thing we can do with this is to take it out, to try to lift the methanator inlet temperature. Certainly ten degrees more on the methanator temperature would I think half the gain CO_2 slip and give us what we are looking for.

Q. Do I understand your flow sheet correctly in that your kick back material is saturated vapor? It's a new vapor?

LIVINGSTONE: The kickback vent - well, the kickbacks of course are normally shut, but the vapor would be saturated? — no, it wouldn't be saturated because the design on the plant is to get to eight degrees at the inlet to the HP case, so it's gas saturated at (8°C) — any kick back gas is kicking back at 19, possibly higher, when you're kicking back actually.

Q. So you are reheating after your knockout?

LIVINGSTONE: In effect yes, that's correct.