

## EFFECT OF IRRIGATION WITH GAS PRODUCED WATER ENRICHED WITH CO<sub>2</sub> ON ALFALFA GROWTH, QUALITY AND MINERAL CONTENT.

By

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### ABSTRACT

Production of gas is accompanied by some quantities of water that differ according to the area. Water produced with gas at Khor laffan, Qatar Gas was analyzed. Also a reasonable amount of CO<sub>2</sub> was also produced which causes some environmental hazards. Effects of irrigation using such water compared to normal water with and without CO<sub>2</sub> was studied on alfalfa (*Medicago Sativa L.*) var. Dabilovare) growth. The plant was grown on polyethylene bags at University of Qatar green house in February 2006. Growth, quality, protein and mineral composition of the crop was analyzed along with soil and water analysis before and after planting.

The results revealed the possibility of using such water in forage production and fit the international standard for Agricultural and within the FAO values. However, the water contained some phenolic compounds which can be eliminated. Enrichment with CO<sub>2</sub> resulted in a positive change in growth parameters (number of leaves / plant, plant height and leaf area ) and increase protein (22.54%,25.33% in the first and the second cut respectively) .The significant effects of mineral content were inconsistent .Further research is needed to be focused on residues taking into account local needs, environmental and production constraints.

**KEYWORDS:** Alfalfa, CO<sub>2</sub>, growth, mineral content, water produced with Gas.

**المخلص:**

يرافق استخراج الغاز كميات من المياه يختلف تركيبها حسب المكنم الغازي وقد وجد من تحليل عينات المياه المأخوذة من أحد آبار منطقة راس لفان يتبع شركة قطر غاز. كما يرافق استخراج الغاز كميات كبيرة من CO<sub>2</sub> يعتبر التخلص منها مشكلة بيئية .

اعتمد هذا البحث على دراسة تأثير الري بالمياه المرافقة لاستخراج الغاز بتركيبها الطبيعي بالمقارنة مع الري بمياه محلاه وذلك بحالتي اشباعها بغاز CO<sub>2</sub> أو بدون ذلك على نمو نبات الجت (*Medicago sativa L.*) صنف دبابلوفيرا الذي زرع ضمن أكياس بولي أثيلين وضعت في البيت الزجاجي التابع لبرنامج العلوم الزراعية بجامعة قطر منذ بداية فبراير 2006 وسجلت متغيرات النمو الخضري لكل قطعة مع تحليل القيمة العلفية ونسبة البروتين والمحتوى المعدني ومتابعة تحليل عينات المياه والتربة قبل وبعد الزراعة .

لقد أشارت النتائج إلى إمكانية استخدام هذه المياه المرافقة لاستخراج الغاز في ري الأعلاف وأنها تتناسب مع المعايير الدولية للمياه المستخدمة في الزراعة وهي ضمن القيم المقبولة بالمقارنة مع جداول منظمة الأغذية والزراعة الدولية مع الإشارة إلى أنها تحتوي بعض المركبات الفينولية التي تم الكشف عنها والتي اقترح عدد من الباحثين طرق للتخلص منها .

وقد أدى اشباع مياه الري بغاز CO<sub>2</sub> إلى تغيرات إيجابية في ظواهر النمو ( عدد الأوراق/ النبات ، طول النبات ، المساحة الورقية ) وفي زيادة نسبة البروتين إلى 22.54% في القطعة الأولى مقابل 25.33% للقطعة الثانية بينما تباينت نتائج تحليل العناصر المعدنية في أوراق الجت في إظهار تأثيرات ذات دلالة معنوية حسب المعاملات المعتمدة . ويقترح استمرار البحث وخاصة ضمن مجال الزراعة المائية للأعلاف في ضوء الأزمات الغذائية التي يشهدها العالم في وقتنا الراهن .

## INTRODUCTION

Rainfall and terrestrial water are always insufficient in arid and semi-arid regions of the World. Ground water is the ultimate alternative source of irrigation under such conditions. The pumpage of ground water is consistently increasing and water withdrawal has exceeded annual recharge. Due to the enhanced use of ground water, many allied problems have also been sprouted<sup>(1)</sup>. The use of other alternative source of water (Treated water) is becoming vital. However, this water should be managed in such a way that the harmful effects are alleviated<sup>(2, 3 and 4)</sup>.

The steady increase in the amount of water used and waste water produced by urban communities and industries throughout the world posses potential health

and environmental problems <sup>(5 and 6)</sup>. Countries are seeking for safe environmentally sound and cost-efficient ways to treat and dispose of waste water. One opportunity is to use municipal waste water (both sewage and industrial effluent) to irrigate forests, forest plantations, greenbelts and amenity trees <sup>(7)</sup>.

Produced water, formation water or brine, as it is sometimes referred to, is comprised of water containing residual hydrocarbons, heavy metals, radionuclide, numerous inorganic species, suspended solids and chemicals used in treated and hydrocarbon extraction <sup>(5)</sup>. Funston, <sup>(7)</sup> added that the installation of waste water treatment plant is the scientific solution to control pollution expected from disposal of produced water. King *et al.* <sup>(3)</sup> agreed that there is a need for policy strategic and programmatic frameworks which facilitate integrated management of land, water and environment.

The use of produced water into irrigation provides a cost effective tool to handle excessive amounts of produced water <sup>(7)</sup>. Before the water can be disposed or reused, it must be purified to a set of specifications for purification and removal of organic and inorganic materials <sup>(5)</sup>. Various advanced separation techniques to remove oil, oily constituents and dissolved solids from the produced water were used <sup>(1,4,5 and 6)</sup>. King, *et al.* <sup>(3)</sup> added that the produced water should not contain any specific ions in concentrations high enough to cause toxicity to plants. However, it is generally not suitable to irrigate with produced water on clay soils without proper management <sup>(8)</sup>.

Ganjero, *et al.* <sup>(1)</sup> found greater electrical conductivity and sodium adsorption ratio (SAR<sub>w</sub>) values than those recommended for irrigation. They concluded that water significantly impacts certain soil properties, particularly if amendments are not properly utilized. Rambeau, *et al.* <sup>(4)</sup> demonstrated the feasibility of utilizing low-salt water (<20g/L) cleaned of hydrocarbons for agricultural or forest irrigation. They tried rudimentary technologies such as artificial wetlands to remove hydrocarbon substances. These results validate the re-use of low-salt produced water in climatic conditions with expected temperature of up to 37c in summer. Carlos *et al.* <sup>(9)</sup>, Kharaka and Rice <sup>(6)</sup> found low salinity but high Silinium and organics in the produced water. They also stated that Cl , Na , Ca were generally the dominant ions , and concentration of Fe , Mn , B , NH<sub>3</sub> and

dissolved organics , including BTEX , phenols and PAH may be relatively high. Karthikeyan and Singh <sup>(10)</sup> added that the mean values of total solids and total dissolved solids were quite high which may cause soil sickness due to poor aeration and higher BOD. However, Li *et al.* <sup>(8)</sup> emphasized that treated water is one of the important resources for agricultural irrigation in regions where are short of fresh water resource.

Gas produced water is normally rich in CO<sub>2</sub> which is essential for plant growth in levels of 1000 to 2000 ppm. Terrestrial ecosystems exchange about 120Gt of carbon per year with the atmosphere, through the process of photosynthesis and respiration <sup>(11)</sup>. Roughly, half of the CO<sub>2</sub> assimilated annually through photosynthesis is released back to the atmosphere by plant respiration <sup>(12 and 13)</sup>. CO<sub>2</sub> dissolved in gas produced water forms carbonic acid (H<sub>2</sub>CO<sub>3</sub>). Enrichment with CO<sub>2</sub> will dramatically increase the growth of green plants. Most plants receive more water and energy, in the form of sunshine than can use. Increasing CO<sub>2</sub> in the growing area will let the plant use the excess water and energy that stored in the leaves. However, Bunce <sup>(14)</sup> and Heath *et al.* <sup>(15)</sup> stated that while small increase in the amount of CO<sub>2</sub> in the water causes lush plant growth. Too much CO<sub>2</sub> can prove to be toxic. Miquel *et al.* <sup>(16)</sup> added that plant tissues are often reduced when plants are exposed to or grown at high CO<sub>2</sub> due to direct effects on enzymes and indirect effects derived from changes in the plants chemical composition.

The present preliminary study was undertaken to generate practicable and economical approaches that help in efficient use of gas-produced water in cropping after alleviating the harmful constituents and maintaining the soil health. Hence, the objective was to evaluate the effects of irrigation with gas produced water on the growth of alfalfa plant.

#### **MATERIALS AND METHODS**

This experiment was conducted at the Glass House, Qatar University, Doha, Qatar in February, 2006. Seeds of alfalfa ( Dabilovare variety ) were tested for germination ( 95.5 % ) and weight ( 0.36 gm/ 100 seeds ). Twenty four Polyethylene bags (30cm X 34cm) were prepared with a mixture of peat-moss and soil which were analyzed before planting. Seeds were sown at a seed rate of 4

grams/m<sup>2</sup>. Four water containers (25 liters) were used to collect water from Ras Gas plant, Ras Laffan , Qatar . Two containers were filled with water produced with gas and two with normal water. Half the containers (One normal and one produced with gas) were enriched with CO<sub>2</sub> in the laboratory, Department of Chemical Engineering, University of Qatar. The pH was adjusted to 5 to 5.5 .The treatments (gas produced water, gas produced water enriched with CO<sub>2</sub>, normal water and normal water enriched with CO<sub>2</sub>) were repeated three times, arranged in the glass house and irrigated when needed.

The plants were detected at early flowering for three cuts. Fresh weight (gm) ,number of leaves per plant , leaf area (cm<sup>2</sup>), plant height (cm) and dry weight (gm) were measured for each cut. Three plant from each replication were dried to measure crude protein and crude fiber. The same dried plants were used to get the plant mineral content. Mixed soil was analyzed before and after planting together with water samples according to Walinga *et al.*<sup>(17)</sup> and Westerman *et al.*<sup>(18)</sup>. Completely Randomized Block Design (CRBD) with three replications was used and analyzed with GENSTST computer program to get the mean separation (LSD).

## RESULTS AND DISCUSSION

Table 1 revealed the analysis of water co-produced with natural gas in Qatar. As shown in the table, gas water contained traces of oil and grease .The PH was lower for water enriched with CO<sub>2</sub>. There were no significant differences on the total dissolved salt (mg/l) for water used with gas water giving the least (161.80 mg/l). The hydrocarbons (HCO<sub>3</sub>) were higher in gas water enriched with CO<sub>2</sub> (130.82 mg/l). CL was higher in gas water and gas water enriched with CO<sub>2</sub> while Br was higher for tap water and tap water enriched with CO<sub>2</sub>. Fe and No<sub>3</sub> were higher for tap water while So<sub>4</sub> was higher for tap water enriched with CO<sub>2</sub> (Table 1).

There was no differences between water types in Ca, K, NH<sub>3</sub> and Sodium Adsorption Ratio (SAR) while Mg and Na were higher for tap water and tap water enriched with CO<sub>2</sub>. Al and Pb amounts were high for gas water and almost the same for other water treatments (Table 1).Cu and Zn amounts were high in gas water enriched with CO<sub>2</sub> and gas water while Fe amounts were high

in water enriched with CO<sub>2</sub>. On the other hand, Mn was high in tap water enriched with CO<sub>2</sub> and tap water. Traces of Cd were observed on tap water and not on gas water.

**Table (1): irrigation water analyses (water co-produced with natural gas in Qatar)\***

Treatments	Gas water + CO <sub>2</sub>	Gas water	Tap water + CO <sub>2</sub>	Tap water	
Oil & Grease mg/l	1.0	1.1	0	0	
pH	5.39	7.12	5.54	7.85	
EC ms/cm	0.30	0.27	0.29	0.28	
Total dissolved salt mg/l	179.1	161.8	175.6	170.7	
Anion	HCO <sub>3</sub> mg/l	130.82	118.36	128.12	110.59
	Cl mg/l	40.78	38.30	31.56	34.40
	SO <sub>4</sub> mg/l	5.43	6.93	11.30	2.98
	F mg/l	0.02	0.05	0.25	0.13
	NO <sub>3</sub> mg/l	0.62	0.24	0.95	0.83
	Br mg/l	3.75	3.63	18.18	20.24
Cation	Ca mg/l	23.25	27.66	26.85	27.45
	Mg mg/l	3.28	2.31	4.26	7.17
	K mg/l	1.43	1.564	1.171	1.564
	Na mg/l	3.28	2.81	4.26	7.17
SAR	0.35	0.34	0.33	0.40	
NH <sub>3</sub> mg/l	4.8	4.5	4.7	3.1	
Trace Elements	Al mg/l	0.01	0.05	0.01	0.01
	Cu mg/l	2.25	1.60	0.25	0.08
	Fe mg/l	2.79	0.69	4.52	5.94
	Mn mg/l	0.10	0.18	0.51	0.22
	Pb mg/l	0.04	0.13	0.05	0.03
	Cd mg/l	0.00	0.00	0.002	0.003
	Zn mg/l	1.01	1.69	0.04	0.06

Properties of the soil used in the experiment before and after sowing were shown in Table 2. The initial soil used contained 87.28% sand, 2% silt, 10.72% clay, 4.33% organic matter, 21.44% field capacity (FC) and 5.9 Cation Exchange Capacity (CEC). The carbonate, PH, EC, HCO<sub>3</sub>, Cl, Na, N, K, Fe, Mn, Al, and Pb amounts were decreased significantly after planting. However, SO<sub>4</sub>, Ca, Mg, K, P, Cu, and Zn amounts were increased with planting (Table 2).

**Table (2) : properties of pot soil before and after planting alfalfa Irrigated with water co-produced with natural gas**

Before planting		Before planting	After planting irrigation					L.S.D	
			Gas water + CO <sub>2</sub>	Gas water	Tap water + CO <sub>2</sub>	Tap water			
							0.05	0.01	
Practical Size Analysis	Clay% (< 0.002 mm)	10.72							
	Silt% (0.002- 0.05mm)	2.00							
	Sand % (0.05- 2 mm)	87.28							
Field Capacity Volumetric %		21.44							
Permanent Wilting Point Vol %		11.16							
Available Water Vol %		10.28							
Organic Matter %		4.33							
Carbonate (CaCO <sub>3</sub> )%		16	14.66	14.66	15.33	15.66	1.15	1.75	
Saturated Water Extraction	pH	7.48	7.71	7.75	7.48	7.57	0.30	0.46	
	EC mS/cm	7.52	7.21	6.59	6.95	7.39	1.36	2.06	
	HCO <sub>3</sub> meq/kg	7.41	3.55	3.36	3.14	2.99	0.61	0.93	
	Cl meq/kg	33.29	24.77	23.08	23.71	29.18	6.08	9.21	
	SO <sub>4</sub> meq/kg	44.58	53.74	48.91	51.33	49.91	14.62	22.14	
	Ca meq/kg	40.53	42.95	37.00	37.99	38.71	10.66	16.15	
	Mg meq/kg	10.21	12.24	11.11	13.00	12.51	2.99	4.53	
	K meq/kg	1.83	4.68	4.92	6.09	5.39	2.27	3.43	
Na meq/kg		32.7	22.20	22.33	21.09	25.46	6.68	10.12	
Cation Exchange Capacity		5.9							
Available Macro & Micro Elements	N %	0.08	0.04	0.03	0.06	0.03	3.47-02	5.26-02	
	P mg/kg	28.24	21.76	32.59	41.20	32.87	13.94	21.11	
	K mg/kg	5.2	1.04	1.19	1.42	1.04	0.47	0.72	
	Cu mg/kg	0.31	0.84	0.74	0.54	0.61			
	Fe mg/kg	11.2	3.75	3.00	3.60	2.74	1.36	2.07	
	Mn mg/kg	4.94	0.88	0.47	0.95	0.40	0.63	0.95	
Zn mg/kg		1.53	4.98	3.77	4.60	2.66			
Total Trace Elements	Al mg/kg	357.80	277.03	242.36	240.36	227.30	48.75	73.85	
	Pb mg/kg	21.4	19.37	18.59	18.68	18.29	1.64	2.84	

Growth quality of alfalfa irrigated with water co-produced with natural gas was shown in (Table 3). The fresh weight of the plant was significantly reduced at irrigation with gas water and gas water enriched with CO<sub>2</sub>. Enriched tap water resulted in the highest fresh weight (16.339/plant). The second and third cuts were significantly better for gas water and tap water respectively. The leaf area was significantly higher for enriched tap and gas water and increased with cuts (Table 3). Number of leaves per plant was significantly higher for tap water than

gas water and increased with cuts. The same trend was noticed in plant height but it was significantly higher with CO<sub>2</sub> than without CO<sub>2</sub>

**Table (3): Growth quality of alfalfa Irrigated with water co-produced with natural gas**

Treatment**	2/4/2006				1/5/2006				21/5/2006				
	Fr. weight	Leaf Area cm <sup>2</sup>	No. of leaves/plant	Plant length cm	Fr. weight	Leaf Area cm <sup>2</sup>	No. of leaves/plant	Plant length cm	Fr. weight	Leaf Area cm <sup>2</sup>	No. of leaves/plant	Plant length cm	
GW+Co2	9.83	11.21	15.88	19.43	9.53	16.66	19.11	21.99	-	-	-	-	
GW	8.93	8.83	16.77	16.42	7.80	12.42	21.44	20.76	-	-	-	-	
TW+Co2	16.33	11.59	24.22	23.51	18.79	32.58	25.66	27.24	35.09	15.23	34.16	35.18	
TW	13.80	10.73	19.11	21.96	11.69	23.02	22.88	29.85	26.00	13.31	27.00	29.56	
L.S.D.	0.05	1.86	1.53	1.73	0.98	0.97	4.34	3.60	4.15	0.74	6.45	11.16	8.39
	0.01	2.81	2.31	2.62	1.49	1.47	6.58	5.46	6.30	1.72	14.88	25.76	19.37

\* Values are mean of analysis of three replications: each one with three plants.

\*\* GW: Gas Water TW: Tap Water

Table 4 showed the quality of the forage under different types of irrigated water. Dry matter was significantly higher for enriched water but there were no significant differences between gas and tap water or between cuts. Crude fiber (CF) was significantly higher for gas water (16.40) while there was no difference between enriched gas and tap water, tap water or different cuts. Crude protein (CP) results showed no significant differences with CO<sub>2</sub> or between cuts but they were significantly higher than without CO<sub>2</sub>.

**Table (4): Forage quality of alfalfa Irrigated with water co-produced with natural gas**

Treatment **	2/4/2006			1/5/2006			21/5/2006			
	Dry Matter	Crude Fiber	Protein	Dry Matter	Crude Fiber	Protein	Dry Matter	Crude Fiber	Protein	
GW + CO <sub>2</sub>	29.20	14.19	22.95	28.20	15.19	22.81	-	-	-	
GW	28.58	16.40	21.34	29.14	15.70	23.29	-	-	-	
TW + CO <sub>2</sub>	29.56	14.80	22.54	29.12	15.25	25.33	29.57	14.85	21.12	
TW	28.88	14.93	20.80	29.50	15.24	20.20	29.32	15.42	22.61	
L.S.D.	0.05	0.28	0.93	1.77	0.56	0.70	-	2.38	2.79	2.43
	0.01	0.43	1.14	2.68	0.84	1.07	-	5.50	6.45	5.61

\* Values are mean of analysis of three replications: each one with three plants.

Plant part for analysis: leaves and shoot.

\*\* GW: Gas Water TW: Tap Water



Results of mineral composition of the forage irrigated with water co-produced with natural gas were illustrated in (Table5). NPK elements showed significant differences between cuts but no consistency among treatments. There was a significant differences between water treatments and always higher with CO<sub>2</sub> enrichment. Na and Cl were higher with CO<sub>2</sub> enrichment but decreased with cuts. However, Ca was higher for enriched tap water but not consistent for the cuts. Mg had the same trend but the amount decreased with cuts. Fe, Cu and Zn amounts were significantly higher with enriched CO<sub>2</sub> and enriched gas water being the highest (Table5).

**Table (5): Mineral Composition of alfalfa Irrigated with water co-produced with natural gas**

		N	P	K	Na	Cl	Ca	Mg	So <sub>4</sub>	Fe	Mn	Cu	Zn
	Treatment	%								Mg/kg			
	First cut	GW + CO <sub>2</sub>	3.67	0.30	2.52	0.44	1.42	2.16	0.37	1.37	48.40	52.05	48.20
GW		3.41	0.27	2.22	0.27	1.72	2.27	0.44	0.61	40.67	59.10	42.03	38.04
TW + CO <sub>2</sub>		3.50	0.24	2.27	0.43	1.45	2.47	0.45	0.41	44.45	51.81	41.22	40.03
TW		3.30	0.25	2.67	0.29	1.67	2.33	0.43	1.58	39.57	49.70	39.22	38.05
Second cut	GW + CO <sub>2</sub>	3.65	0.23	2.26	0.34	1.42	2.04	0.24	0.29	24.02	58.97	45.10	40.30
	GW	3.73	0.23	2.38	0.29	1.15	2.40	0.35	0.26	27.24	52.06	43.45	37.50
	TW + CO <sub>2</sub>	4.05	0.26	2.71	0.35	0.84	2.36	0.33	0.20	27.03	36.73	39.11	39.61
	TW	3.23	0.24	2.70	0.28	0.58	2.52	0.29	0.28	32.26	58.72	40.12	38.30
Third cut	TW + CO <sub>2</sub>	3.38	0.29	2.33	0.24	0.69	2.27	0.38	0.19	29.84	37.14	37.77	42.41
	TW	3.62	0.29	2.34	0.26	1.09	2.22	0.43	0.22	30.47	41.20	39.89	40.47
L.S.D.	Cut time 0.05	0.13	0.019	0.071	0.042	0.096	0.094	0.018	0.037	2.04	1.11	1.89	0.88
	Cut time 0.01	0.17	0.025	0.097	0.057	0.131	0.127	0.024	0.050	2.77	1.51	2.58	1.20
	Treatment 0.05	0.15	0.021	0.082	0.049	0.111	0.180	0.020	0.043	2.35	1.28	2.19	1.02
	Treatment 0.01	0.20	0.029	0.111	0.066	0.151	0.147	0.028	0.058	3.20	1.74	2.95	1.39
	Interaction 0.05	0.26	0.037	0.142	0.084	0.193	0.187	0.035	0.074	4.07	2.22	3.79	1.77
	Interaction 0.01	0.35	0.050	0.193	0.115	0.262	0.255	0.048	0.100	5.53	3.01	5.16	2.40

The results showed that alfalfa was affected when irrigated with water co-produced with gas. The water contained traces of oil and grease and some other compounds which can be eliminated. However, the water fit the international standard for agriculture and within the FAO values for irrigation. King *et al.* <sup>(3)</sup> stated that there is a need for policy strategic and programmatic frameworks

which facilitate integrated management of land, water, and environment. As shown in Tables 3 and 4 , the produced water can result in a reasonable production with acceptable quality . This was in line with Funston *et al.* <sup>(7)</sup> who stated that the conversion of produced water into irrigation provides a cost effective tool to handle excessive amounts of produced water. Treatment of gas produced water before irrigation and enrichment with CO<sub>2</sub> will reduce the problems. Salmon *et al.* <sup>(5)</sup> added that before the water can be disposed of or reused, it must be purified to a set of specifications for purification and removal of organic and inorganic materials. Further work is needed to focus on residues taking into account local needs, environmental and production constraints.

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