Development of a Hydrothermal Multi Input Flow-through a Water-Gas-Rock Reactor for Geothermal Non-Condensable Gas Injection Reaction Testing

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ABSTRACT

A flow-through multi-input chemical-water-gas-rock reactor for geothermal non-condensable gas (NCG) reinjection testing is in the final stages of the commissioning process at The University of Auckland. This apparatus can react simulated geothermal brines with gas supplied via a pressurised dissolution column and up to two secondary chemical inputs supplied via high-pressure, low-flow metering pumps with rock or any other solid material at temperatures up to 230ºC and pressure up to 30 bar (gauge). At temperature below 155ºC, this apparatus can constantly monitor solution pH via a high pressure and temperature-rated pH electrode. An additional feature of this system is the ability to obtain grab samples at reaction temperature and pressure, without the need for a sample cooling, which has the advantage of retaining all components of the reaction solution in the sample, which may otherwise precipitate and deposit within cooling and pressure regulation equipment. Although this equipment is initially intended to test methods of NCG injection into geothermal reservoir rock, this apparatus also has significant potential to simulate many other natural and industrial hydrothermal and geothermal physicochemical processes.

1. INTRODUCTION

The purpose of this paper is to provide a description and some potential applications of a hydrothermal Multi Input Flow Through water-gas-rock Reactor (MIFTR) currently being constructed by the Department of Engineering Science at The University of Auckland. MIFTR can react multiple input phases with solid samples at elevated pressure and temperature, with the capability to react four separate solid samples in separate pressure chambers simultaneously with injected fluid phases. MIFTR shares many common features with apparatus developed by other experimentalists for mass transfer style water-rock experiments previously, such that of Okamoto et al. (2010), Sonney and Mountain (2013), Mountain and Sonney (2011), Sonney and Mountain (2013), Passarella et al. (2017), Orywall et al. (2017), and Ma et al. (2018) (Table 1), however MIFTR also has a number of novel features and unique functionalities. This apparatus is being developed as part of the Reversing Carbon Emissions in the "Geothermal Energy Industry: Template for Emission-Intensive Industries" project; however, this equipment is anticipated to have significant applications beyond the scope of this research.

While many static/non-flowing, simple autoclave-based hydrothermal water-rock (±gas) experiments have been conducted over the decades, comparatively few flow-through style apparatuses have been developed for this same purpose. Static/non-flowing style experiments are ideal for studying many geothermal processes, particularly where geochemical equilibrium relationships are to be determined. However, where mass transport forms an important system component, a more complex flow-through experimental apparatus becomes necessary.

All flow-through water-rock hydrothermal experimental apparatus share some common features and a general component arrangement (Figure 1A and B). Firstly, a reactant solution(s) is introduced into the system using a high-pressure, low-flow (from ≪1 to 50 mL/min) pump(s). The pump/s can either draw in the reactant solution directly (Fig 1A) or use a separate inert working fluid to displace a piston in a separate pressure vessel, forcing the reactant solution through the apparatus (Figure 1B). The advantage of this latter configuration is that any potential corrosive fluids do not come into contact with the pump internals. Once introduced into the apparatus, the fluid is heated and passed into a temperature-controlled vessel, where it reacts with the solid component in the solid-solution pair under study. The resulting reacted effluent then passes through a fluid cooler to prevent boiling following depressurisation via a back pressure control valve to ambient pressure. Measurements such as pH and conductivity can be taken at this point from the cooled and depressurised effluent, along with samples for later chemical analysis.

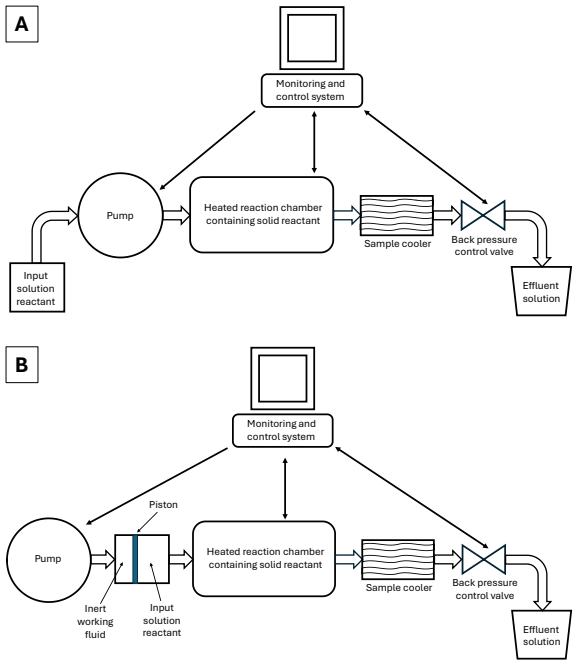

Figure 1: Schematic representation of common features and general component arrangement of flow-through, water-rock, hydrothermal experimental apparatus.

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Table. 1 Comparison of features, operation and capabilities of hydrothermal fluid-rock reactor apparatus referenced in this report.

Institute	Temperature Capability	Temperature Control	Pressure capability	Pressure Control	Fuid flow rate mL/min	Fluid Reactant Addition Method	Fluid Sampling	Fluid pH Measurement	References
GNS Science, New Zealand (Figure 2, diagram A)	Up to 700°C	Pressure vessel and tubing heated in oven	Up to 290 bar	Digitally-controlled active back pressure regulator	0.001–15	Single fluid reactant via single pump (piston), inert working fluid with isolating piston	End circuit cooled effluent	End circuit cooled effluent (corrected to reaction conditions using PHREEQC)	Sonney and Mountain(2013), Rendel and Mountain (2023)
Jilin University, China (Figure 2, diagram B)	Up to 430°C	Exposed autoclave with clamp on self insulated ring heater	Up to 400 bar	Mechanical back pressure valve with separate confining pressure pump	0.00001 to 45	Single fluid reactant via dual parallel (syringe) pumps, inert working fluid with isolating piston	End circuit cooled effluent	End circuit cooled effluent	Ma et al. (2018)
Institute of Nuclear and Energy Technologies, Germany (Figure 2, diagram C)	Up to 150°C	Fluid preheated in tubing via wire heaters, autoclave insulated only	Up to at least 400 bar	Mechanical back pressure valve with separate confining pressure pump	2.0-20	Two fluid reactant via two (type not stated) pumps, inert working fluid (isolation mechanism unclear)	End circuit cooled effluent	End circuit cooled effluent	Orywall et al. (2018)
Tohoku University, Japan (Figure 2, diagram D)	Up to at least 430°C	Insulated tubular vessel with 3 stages of wire heaters	Up to at least 300 bar	Mechanical back pressure valve with separate confining pressure pump	1.00	Single fluid reactant via single (type not stated) pump in direct contact with reactant	End circuit cooled effluent	End circuit cooled effluent	Okamoto et al. (2010)
University of Auckland, New Zealand (this study)	Up to 230°C (limited by PEEK valve seats)	Fluid (preheat), reactors and sample cylinders) directly heated via wire heaters (dual stage)	Up to 65 bar (instrumentation limited)	Digitally-controlled active back pressure modulation valve	0.01-125	Three stage (separate) fluid reactant addition via three (piston HPLC) pumps in direct contact with reactants	Online grab sample cylinders at reaction temperature and pressure	Online at system pressure and temperature (up to 155°C) either before or after reaction vessels	This study

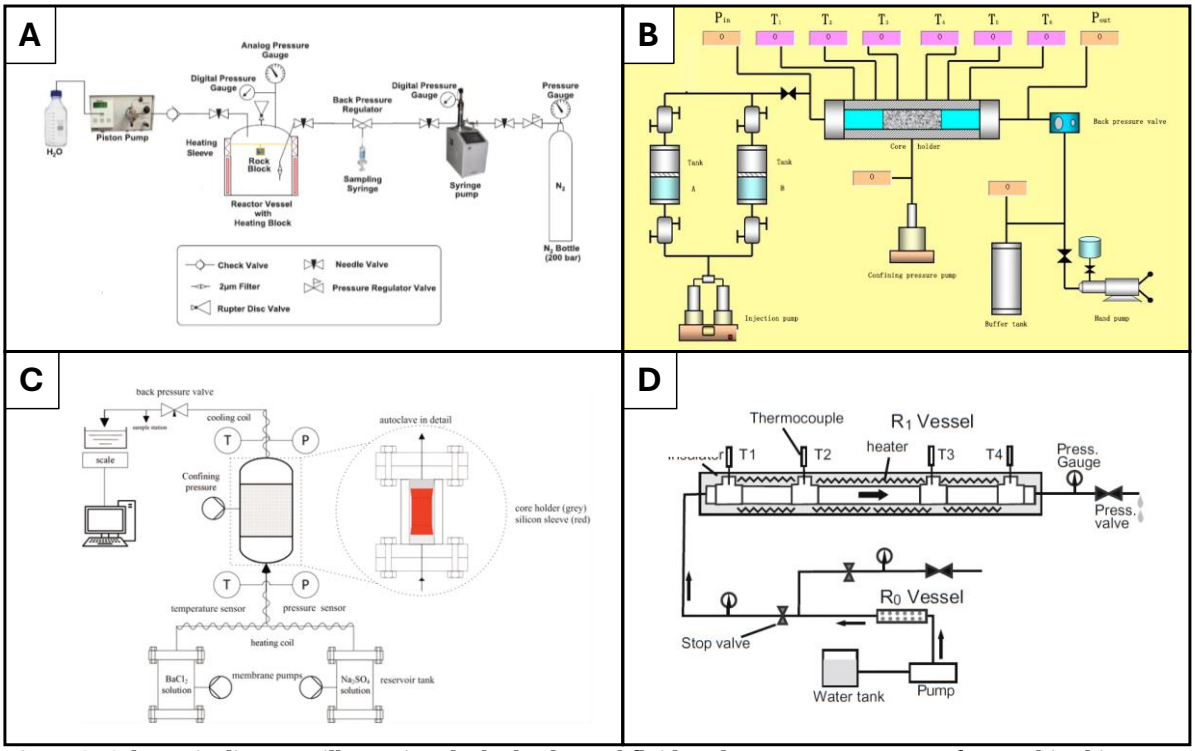

Figure 2: Schematic diagrams illustrating the hydrothermal fluid-rock reactor apparatus referenced in this report. Diagrams adapted from each of the papers referenced. A: Rendel and Mountain (2023); B: Ma et al. (2018); C: Orywall et al. (2018); D: Okamoto et al. (2010).

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Beyond these basic commonalities, there is a large scope for the addition of extra features and capabilities to tailor hydrothermal experiment apparatus to achieve the aims of the study. Some general features and capabilities of several notable examples of hydrothermal water-rock reaction experimental apparatus are compared in Table 1 and Figure 2. MIFTR expands upon the functionality of other similar apparatus in several ways. Among these, the ability to inject 3 different liquid reagents and one gas mixture into the fluid stream simultaneously, measure pH at system pressure and temperature (up to 155 °C) before or after the four parallel reaction vessels, and obtain fluid grab samples at reaction pressure and temperature. Conversely, in its current iteration MIFTR is not capable of the high temperatures and pressures of some of the other apparatus outlined in Table 1 and Figure 2, with MIFTR being limited to a maximum operating pressure of 30 bar (gauge) (maximum pressure rating of pH electrode) 230ºC (maximum rating of PEEK valve seats). Nonetheless, these temperature and pressure limitations are sufficient for studying shallow natural hydrothermal processes and those affecting geothermal reinjection wells, which are the dominant areas of interest for this research. Additionally, due to the modular nature of the apparatus, these components can be easily upgraded to extend these current limitations if desired in the future.

2. MIFTR DETAILS

2.1 General

Given the unique functionalities required and practical industrial research applications of the Template for Emission-Intensive Industries project for which MIFTR is primarily being developed, relatively standard industrial 'off the shelf' components have been used to construct MIFTR where at all possible. For instance, except for the gas dissolution column and fluid delivery pumps, all pressure components and valves have been sourced from Swagelok™. Similarly, instrumentation and control is provided by an adapted Walchem Intuition 9™ water treatment controller. A modular approach has also been taken in the development of MIFTR. This allows a large degree of adaption and improvement of MIFTRs capabilities over time and makes the system relatively portable. Although nearly all of the components utilised in the design of MIFTR are standard industrial process items, all pipe work, electrical work, supporting structures, necessary modifications to the components, and process design have been completed by the author.

2.2 Apparatus Control

The Walchem Intuition 9™ as configured for MIFTR features 12 relay-operated outputs, four powered (24VDC) and eight switched only, two analogue outputs (4-20mA), and 12 analogue (4-20mA) inputs. As configured, this allows for monitoring and logging all 12 MIFTR instrumentation channels, comprising six temperature transmitters, four pressure transmitters, pH and CO2 mass balance. Walchem Intuition 9™ allows TR to operate with three separately controlled heating stages, closed-loop back pressure control, and four reactor tube control valves, with scope for closed-loop pH control and a further five relay-controlled functions. In terms of a user interface, the Walchem Intuition 9™ features both a touch screen control and graphical user interface (GUI) when connected to a PC with a WIFI and ethernet connection, allowing monitoring and alteration of MIFTR operation parameters remotely.

2.3 Fluid reactant addition

Like other hydrothermal water-rock reactor apparatus discussed in this report, MIFTR uses high-pressure, low-flow capable metering pumps. Three High-Performance Liquid Chromatography (HPLC) pumps manufactured by Additive Systems Inc™. (ASI™) are utilised by MIFTR for this purpose. These high-precision metering pumps have a dual piston design and may be operated in isocratic or gradient modes. The primary fluid delivery pump (Pump 1) can deliver a precise metered fluid flow of between 0.01 mL/min 125mL per minute with a head pressure of up to 100 bar. This pump delivers the primary reactant fluid, such as water or geothermal brine. Meanwhile, the two secondary reagent dosing pumps (Pumps 2 and 3) can deliver a metered fluid flow of between 0.0005 and 4 mL/min with a head pressure of up to 470 bar. These two supplementary dosing pumps can be used to simulate many geothermal plant chemical processes such as brine acid injection, steam condensate mixing with separated brine, non-condensable gas (NCG) injection, and antiscalant dosing at a reinjection wellhead.

2.4 CO_2 dissolution column

CO2 is introduced into the dissolution column via 0-34.4 bar regulator from a swapable bottle. This apparatus operates in a fluid-gas counterflow fashion where CO_2 is vertically sparged into the vessel's base, and the fluid reactant is introduced at the top of the vessel. The vessel is packed with 5mm diameter spherical inert ceramic beads to aid with gas-fluid contact and, hence, gas dissolution. CO_2 charged reactant then exits the base of the vessel, with the outlet isolated for the gas flow path via an internal baffle.

2.5 Pressure control

Due to the large range in metered flow-rate magnitude that the ASI™ solution delivery pumps are capable of and the small total liquid volume delivery rates involved, a digitally controlled back pressure modulation valve is required to maintain pressure stability when MIFTR is operating. After some early testing utilising a single large pressure vessel, a simple mechanical back pressure regulator was found to be unable to operate effectively with the low fluid flow rates required for the operation of the MIFTR apparatus. A Swagelok™ severe service needle valve fitted with a Hanbay™ electronic modulation actuator is now being utilised to address this. This valve, and hence back pressure across the MIFTR experimental apparatus, is operated by the Walchem Intuition 9™ controller, with the signal output from the pressure transmitter (PT) utilised by the Walchem Intuition 9™ controller maintaining the MIFTR apparatus pressure setpoint. The purpose of PT1, PT2, and PT3 is to monitor the differential pressure across the inline post-reagent dosing inline filters, which are used to aid with reagent mixing, with the outputs from PT3 and PT4 also used to monitor differential pressure across the water-rock reactor tubes.

2.6 Temperature control

Temperature is controlled across 3 separate zones. Firstly, a preheating zone where the two secondary reagents are dosed and mixed with the primary fluid flow, secondly the only pH measurement assembly and associated valving, and thirdly the reactor tube and fluid sample cylinder assembly.

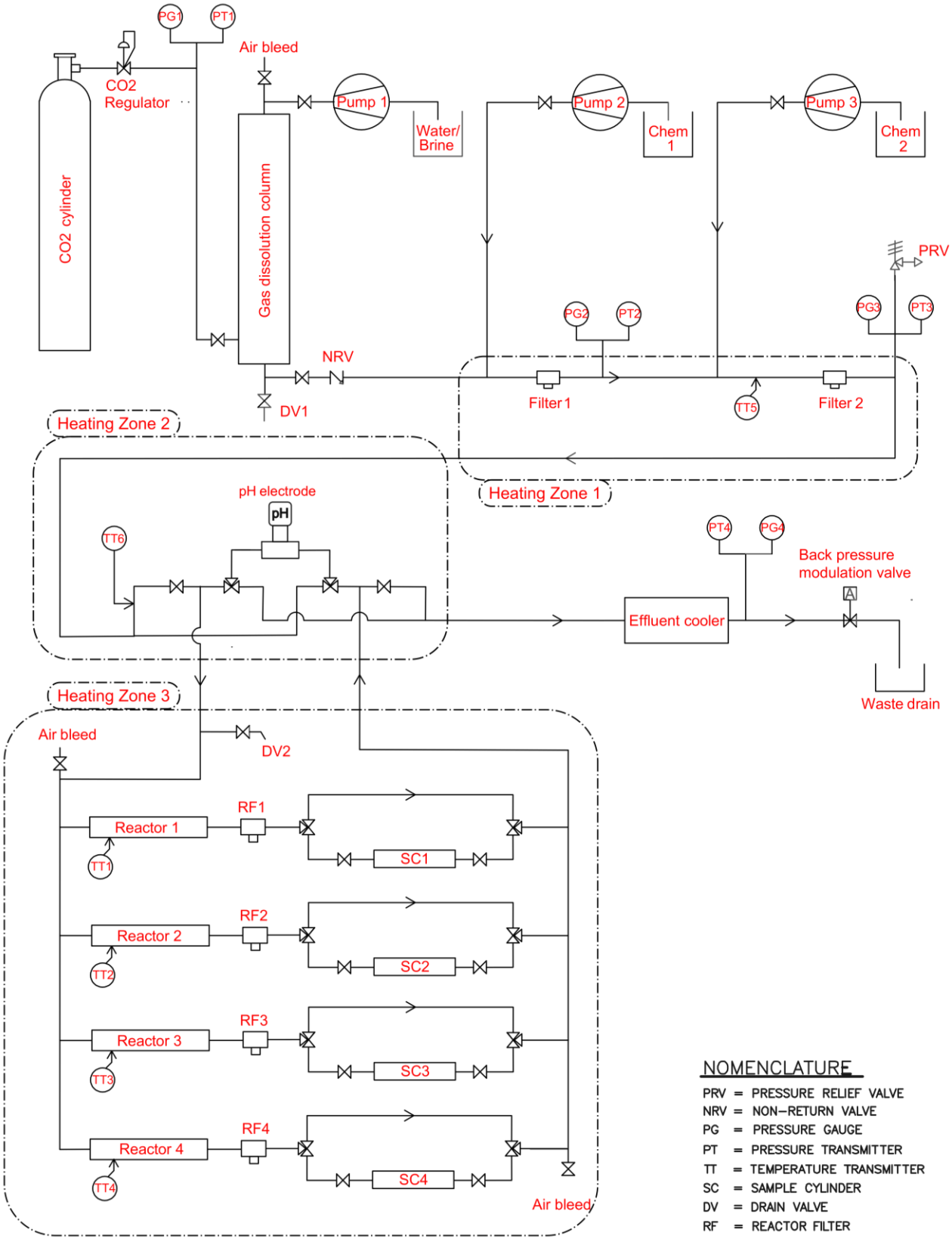

Figure 3: Schematic diagram of the MIFTR experimental apparatus.

This arrangement allows for a wide range of potential for experiment design and the ability to step the temperature up within the reactor and assembly sampling beyond the 155°C limit of the online pH electrode.

Heating of the components is achieved using small diameter mineral insulated metal sheath (MIMS) elements custom bent as required and clamped to the 316 Stainless steel tubing and pressure components of MIFTR. These heated components are then insulated with a calcium silicate furnace insulation blanket finished with aluminium cladding.

2.7 pH measurement

MIFTR uses a Rosemount Analytical PERpH-X™ model 3300HT which is capable of operating at up to 155°C and 30 bar_g. The signal is processed by a Rosemount™ Model 1056 Dual Input Intelligent Transmitter, which outputs a 4-20mA signal to the Walchem Intuition 9™ controller and facilitates autocalibration of the electrode. MIFTR can monitor fluid pH before or after the fluid passes through the water-rock tubes, selectable via a valve assembly. These valves may also be set to allow the pH electrode to be bypassed for experiments at pressures greater than 30 bar_g or for cleaning, calibration, and general maintenance without requiring MIFTR to be shut down.

2.8 Reactor vessels

MIFTR can operate up to four separate water-rock reaction vessels simultaneously. To ensure a known mass of fluid is passed through each reactor, there is an electronically operated valve for each reactor tube, with only one valve open at a time and operating in a rolling sequence. The operation of each valve actuator can be set independently of the others, which allows different effective volumes of fluid to be passed through each water-rock reactor within the same experimental run. This effectively allows for four different experiments (with the same fluid chemistry) to be conducted simultaneously.

In contrast with other hydrothermal water-rock reactor apparatus, the MIFTR water-rock reactor vessels are very simply formed from 5/8" OD, 0.65" wall thickness 316 stainless steel tube. Each reactor tube is 150mm long and oriented vertically, with a cylindrical sintered stainless steel filter crimped into the lower (outlet) end. This effectively makes the reactors disposable, which allows them to be cut longitudinally or sectioned after the experiment as required for analytical purposes. Another 150mm length of stainless-steel tube, two Swagelok™ 5/8" ferrule sets and a stainless-steel filter are all needed to form a new reactor vessel. All fabrication required to produce these can be carried out in the laboratory within minutes.

2.9 Fluid sampling

Also unique to MIFTR is that fluid grab samples can be obtained directly after the water-rock reactor tubes without cooling or depressurising the fluid through the back pressure modulation valve. To achieve this, each water-rock reactor tube has a dedicated sample cylinder, which can be run in line with the reactor (Figure 3), or bypassed via a separate tube by operating two 3-way valves. Fluid is passed through the sample cylinders by default when MIFTR is operating, with the relevant pair of 3-way valves set to bypass the cylinder when removing it to obtain a grab sample. Once a cylinder is removed for sampling, it is cooled in a water bath for 10 minutes before being discharged into a sample container. After this, 5 mL of 68% v/v HNO_3 is used to rinse the cylinder of any material which may have precipitated during the cooling of the sample cylinder. This acid solution is then also emptied into the sample container, which serves to preserve the sample before it is analysed. The cylinder is then rinsed and then filled with ultrapure water. The cylinder is then placed in a small oven to bring its temperature close to the experiment temperature before being reinstalled into the reactor tube heating assembly.

3. POTENTIAL APPLICATIONS

MIFTR offers a wide variety of applications to both academia and industry. MIFTR is primarily being developed for the "Geothermal Energy Industry: Template for Emission-Intensive Industries" project, which is investigating means for reversing carbon emissions in the geothermal energy industry, however, it has significant potential in many other areas of geothermal research. Given the nature of the project for which MIFTR has been designed, an obvious area of utilisation is determining the impacts of NCG injection into waste brine on rocks hosting reinjection wells. Additionally, due to the ability of MIFTR to inject multiple reagents at different process stages, it is also possible to test the effectiveness of antiscalant agents on formation injectivity prior to them being deployed in the field. Additional uses include hydrothermal rock alteration experiments. The ability of MIFTR to effectively run four experiments simultaneously greatly reduces data acquisition time. This feature also allows for different solid samples to be exposed to precisely the same physicochemical conditions, providing an extremely robust comparison of results. Another exciting possibility is the potential of MIFTR to further the understanding of the hydrothermal processes and conditions influencing the deposition of valuable minerals and potentially aid in developing methods for their industrial recovery.

4. CONCLUSION

The ongoing development of MIFTR at the University of Auckland represents a significant resource for supporting both academic and industrial research into natural and industrial geothermal processes. By offering the ability to simulate complex, multi-step geothermal processes, MIFTR opens up many exciting new experimental possibilities in the geothermal research space. Its modular design and the capacity to conduct simultaneous experiments under varying conditions allow for more efficient data collection and robust comparative analysis. The reactor's primary application in exploring non-condensable gas reinjection into geothermal reservoirs addresses a critical challenge in the geothermal energy industry. However, MIFTR's versatility extends its utility beyond this project, enabling detailed studies on hydrothermal alteration, antiscalant testing, and mineral deposition processes. With its unique features, such as real-time pH monitoring and the ability to capture high-quality fluid samples at reaction conditions, MIFTR is well-positioned to contribute to advancing geothermal science and developing innovative solutions for the energy sector.

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